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(54) Title: FIELD EMISSION DEVICES USING MODIFIED CARBON NANOTUBES

(57) Abstract: The present invention relates to a field emission device comprising an anode and a cathode, wherein said cathode includes carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment. The present invention also relates to a field emission cathode comprising carbon nanotubes which have been subject to such treatment. A method for treating the carbon nanotubes and for creating a field emission cathode is also disclosed. A field emission display device containing carbon nanotube which have been subject to such treatment is further disclosed.



**WO 03/084865 A2**

## **Field Emission Devices Using Modified Carbon Nanotubes**

This application claims the benefit of U.S. Provisional Application No. 60/298,193, filed June 14, 2001, hereby incorporated by reference.

### **Field of Invention**

The present invention relates to field emission cathodes which use carbon nanotubes.

### **Background of the Invention**

Field emission devices are devices that capitalize on the movement of electrons. A typical field emission device includes at least a cathode, emitter tips, and an anode spaced from the cathode. A voltage is applied between the cathode and the anode causing electrons to be emitted from the emitter tips. The electrons travel in the direction from the cathode to the anode.

These devices can be used in a variety of applications including, but not limited to, microwave vacuum tube devices, power amplifiers, ion guns, high energy accelerators, free electron lasers, and electron microscopes, and in particular, flat panel displays. Flat panel displays can be used as replacements for conventional cathode ray tubes. Thus, they have application in television and computer monitors.

Conventional emitter tips are made of metal, such as molybdenum, or a semiconductor such as silicon. The problem with metal emitter tips is that the control voltage required for emission is relatively high, e.g., around 100 V. Moreover, these emitter tips lack uniformity resulting in non-uniform current density between pixels.

More recently, carbon materials, have been used as emitter tips. Diamond has negative or low electron affinity on its hydrogen-terminated surfaces. Diamond tips, however, have a tendency for graphitization at increased emission currents, especially at currents about thirty mA/cm<sup>2</sup>. Carbon nanotubes, also known as carbon fibrils, have been the latest advancement in

emitter tip technology. Although much work has been done in the area of carbon nanotubes as emitter tips in field emitting technologies, substantial improvement is still needed, specifically, in three areas. These areas are reducing work voltage, increasing emission current, and increasing emission sites.

Reducing the work voltage increases the ease of electron emission and also increases the longevity of the emitter tips. Increasing both the emission current and the number of emission sites increase the brightness.

### **Objects of the Invention**

It is an object of the present invention to provide improved field emission cathodes comprising carbon nanotubes as the emitters, which operate at reduced working voltage, have increased emissions and more emission sites.

It is a further object of this invention to provide improved field emission cathodes where the emitters comprise treated carbon nanotubes.

It is yet a further object of this invention to provide methods for manufacturing improved field emission cathodes by screen or ink-jet printing of substrates with inks containing treated or untreated carbon nanotubes.

It is still a further object of this invention to provide improved field emission display devices having improved properties such as reduced working voltage, increased emissions and more emission sites.

### **Summary of the Invention**

The present invention relates to a field emission cathode comprising carbon nanotubes, wherein the nanotubes have been subjected to an energy, chemical, plasma or mechanical

treatment. The carbon nanotubes may form the cathode or may be deposited onto a substrate to form the cathode.

This invention also relates to a field emission device comprising an anode and a cathode which has been subject to such a treatment.

In one embodiment, the field emission device comprises a substrate, a porous top layer positioned on said substrate, a catalyst material positioned on said layer and a cathode positioned on said catalyst material, said cathode including a bundle of carbon nanotubes which have been subjected to a treatment as described above.

The present invention also includes various field emission display devices. In one embodiment, the field emission display device comprises a first substrate, a first metal film on said first substrate; a conductive polymer film on said first metal film, said conductive polymer film including emitter tips comprising carbon nanotubes which have been subject to a treatment as described above; a dielectric film on said first metal film; a second metal film on said dielectric film; a spacer; a transparent electrode separated from said second metal film by said spacer; a fluorescent material on one side of said transparent electrode; a second substrate on the other side of said transparent electrode; and a power supply.

In an alternative embodiment, the field emission display device comprises a cathode including carbon nanotubes which have been subjected to a treatment as described above; an insulating layer on said cathode; a gate electrode on said insulating layer; an anode spaced from said cathode comprising a phosphor layer, an anode conducting layer and a transparent insulating substrate; and a power supply.

The carbon nanotubes used in the cathodes and field emission devices of the invention may be single wall or multi-wall. They comprise substantially cylindrical carbon fibrils having

one or more graphitic layers concentric with their cylindrical axes, are substantially free of pyrolytically deposited carbon overcoat, have a substantially uniform diameter between 1 nm and 100 nm and have a length to diameter ratio greater than 5. The carbon nanotubes may be in form of aggregates such as cotton candy aggregates or bird nest aggregates, as well as in the form of a mat or a film.

Energy treatments may include ion beams, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam. Plasma treatment may be performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof. Chemical treatment may include acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

The field emission cathode may be formed by dispersing carbon nanotubes into a liquid vehicle to form a solution; transferring said solution to an electrophoresis bath, said bath including an anode and a cathode immersed therein; applying a voltage to said anode and said cathode, thereby causing said carbon nanotubes to deposit onto said cathode; removing said cathode from said bath; heating said cathode; and subjecting such cathode to a treatment as described above.

### **Brief Description of the Drawings**

The accompanying drawings, illustrate an exemplary embodiment of the present invention.

Figure 1 is a cross-sectional view of a field emission display device using an modified carbon nanotube cathode according to an exemplary embodiment of the present invention;

Figure 2 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 3 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 4 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 5 illustrates an electrophoresis bath used to fabricate a carbon nanotube film (electrode);

Figure 6 illustrates another electrophoresis bath used to fabricate a carbon nanotube film (electrode);

Figure 7 illustrates a schematic to measure the differences between treated (modified) and untreated field emission characteristics;

Figure 8 is a plot showing cathode current as a function of voltage for modified carbon nanotubes versus untreated nanotubes in a field emission device;

Figure 9 is a Fowler-Nordheim plot for modified carbon nanotubes and untreated nanotubes in a field emission device.

Figure 10 illustrates a classical field emitter;

Figure 11 illustrates a field emitting device using ion bombarded carbon nanotubes;

Figure 12 is a SEM view of the carbon nanotubes on the aluminum substrate.

Figure 13 illustrates a carbon nanotube mat;

Figure 14 illustrates the electron emission behavior of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats in the form of plots of current density as a function of the electric field.

Figure 15 is a series of photographs of electron emission patterns of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats.

Figure 16 is a series of plots of emission characteristics of inkjet printed carbon nanotubes.

Figure 17 is a series of photographs of electron emission patterns from sample inkjet printed carbon nanotubes.

Figure 18 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-01.

Figure 19 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-02.

Figure 20 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-04.

Figure 21 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-68-01.

### **Detailed Description of the Invention**

All referenced patents, patent applications, and publications are incorporated by reference herein.

### **Definitions**

“Aggregate” refers to a microscopic particulate structures of nanotubes.

“Assemblage” refers to nanotube structures having relatively or substantially uniform physical properties along at least one dimensional axis and desirably having relatively or substantially uniform physical properties in one or more planes within the assemblage, i.e. having isotropic physical properties in that plane. The assemblage can comprise uniformly

dispersed individual interconnected nanotubes or a mass of connected aggregates of nanotubes. In other embodiments, the entire assemblage is relatively or substantially isotropic with respect to one or more of its physical properties.

“Carbon fibril-based ink” refers to an electroconductive composite in which the electroconductive filler is carbon fibrils.

“Graphenic” carbon is a form of carbon whose carbon atoms are each linked to three other carbon atoms in an essentially planar layer forming hexagonal fused rings. The layers are platelets having only a few rings in their diameter or ribbons having many rings in their length but only a few rings in their width.

“Graphenic analogue” refers to a structure which is incorporated in a graphenic surface.

“Graphitic” carbon consists of layers which are essentially parallel to one another and no more than 3.6 angstroms apart.

“Nanotube”, “nanofiber” and “fibril” are used interchangeably. Each refers to an elongated hollow carbon structure having a diameter less than 1  $\mu\text{m}$ . The term “nanotube” also includes “bucky tubes” and graphitic nanofibers in which the graphene planes are oriented in herring bone pattern.

The terms “emitter tips” and “emitters” are interchangeable. The use of the word “tip” is not meant to limit the emission of the electrons only to the tips of the carbon nanotubes. The electrons can be emitted from any part of the carbon nanotubes.

### **Carbon Nanotubes**

Carbon nanotubes (CNTs) are vermicular carbon deposits having diameters of less than five hundred nanometers. They exist in a variety of forms, and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces, by high



temperature carbon arc processes, where solid carbon is used as the carbon feed stock, and by simultaneous laser vaporization of graphite rods and a transition metal. Tennent, U.S. Patent No. 4,663,230, succeeded in growing small diameter nanotubes having cylindrical ordered graphite cores and an ordered "as grown" graphitic surface uncontaminated with pyrolytic carbon. Tennent, describes carbon nanotubes that are free of a continuous thermal carbon overcoat and have multiple graphitic outer layers that are substantially parallel to the fibril axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the curved layers of graphite, substantially perpendicular to their cylindrical axes. They generally have diameters no greater than 0.1 micron and length to diameter ratios of at least five. Such nanotubes having graphitic layers that are substantially parallel to the fibril axis and diameters between 3.5 and 75 nanometers, are described in Tennent et al., U.S. Pat. No. 5,165,909 and Tennent et al, U.S. Pat. No. 5,171,560.

The graphitic planes may also be oriented at an angle to the fibril axis. Such structures are often called "fishbone" fibrils or nanotubes because of the appearance of the two dimensional projection of the planes. Such morphologies and methods for their production are discussed in U.S. Patent No. 4,855,091 to Geus, hereby incorporated by reference.

Assemblages and composites consisting of multiwall nanotubes have been described in Tennent et al, U.S. Patent No. 5,691,054. Such assemblages and composites are composed of randomly oriented carbon fibrils having relatively uniform physical properties. Furthermore, these multiwall nanotubes are substantially free of pyrolytically deposited carbon.

The carbon nanotubes disclosed in U.S. Patents Nos. 4,663,230, 5,165,909, and 5,171,560, may have diameters that range from about 3.5 nm to 70 nm and lengths greater than 100 times the diameters, an outer region of multiple essentially continuous layers of ordered

carbon atoms and a distinct inner core region. Simply for illustrative purposes, a typical diameter for a carbon fibril may be approximately between about 7 and 25 nm, and a typical range of lengths may be 1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

As disclosed in U.S. Pat. No. 5,110,693 and references therein, two or more individual carbon fibrils may form microscopic aggregates of entangled fibrils. These aggregates can have dimensions ranging from 5 nm to several cm. Simply for illustrative purposes, one type of microscopic aggregate ("cotton candy or CC") resembles a spindle or rod of entangled fibers with a diameter that may range from 5 nm to 20  $\mu\text{m}$  with a length that may range from 0.1  $\mu\text{m}$  to 1000  $\mu\text{m}$ . Again for illustrative purposes, another type of microscopic aggregate of fibrils ("birds nest, or BN") can be roughly spherical with a diameter that may range from 0.1  $\mu\text{m}$  to 1000  $\mu\text{m}$ . Larger aggregates of each type (CC and/or BN) or mixtures of each can be formed.

Recently carbon nanotubes having a single wall comprising graphite have been produced. These single wall carbon nanotubes have been described in Bethune et al., U.S. Pat. No. 5,424,054; Guo, et al., Chem. Physics Lett., 243:1-12 (1995); Thess, et al, Science, 273:483-487 (1996); Journet et al., Nature 388 (1997) 756; Vigolo, et al., Science 290 (2000) 1331. They are also described in U.S. Patent Application Serial No. 08/687,665, entitled "Ropes of Single-Walled Carbon Nanotubes" herein incorporated by reference.

Additional methods of producing single wall nanotubes production have been described in PCT Application No. PCT/US99/25702 and PCT Application No. PCT US98/16071 herein incorporated by reference.

Single wall nanotubes are useful in a variety of applications. The tubular structure imparts superior strength, low weight, stability, flexibility, thermal conductivity, large surface area and a host of electronic properties. They can be used as reinforcements in fiber reinforced

composite structures or hybrid composite structures, i.e., composites containing reinforcements such as continuous fibers in addition to single wall nanotubes.

The carbon nanotubes may be treated in their as-made form or may be deposited as a film on a suitable substrate and then treated.

### **Preparation of Films Containing Carbon Nanotubes**

The carbon nanotubes used were obtained from Hyperion Catalysis International, Cambridge Mass. They had the designations #1100 and #1100 L. Sample #1100 L comprised carbon nanotubes having a so-called BN macromorphology that had been ball milled in a Red Devil Shaking Ball Mill for approximately four hours. Some samples were treated with an acid wash of twelve grams of  $\text{H}_3\text{PO}_4$  in 1.5 liters of water at atmospheric reflux before ball milling. The carbon nanotubes were dried in an oven before ball milling.

### **The Solution of Nanotubes**

The nanotubes were dispersed by known methods in a suitable solvent as is well known in the art, e.g. isopropyl alcohol.

### **The Substrate**

Aluminum substrates were prepared by vapor depositing aluminum onto glass flats that were approximately 55 mm x 45 mm x 1 mm in its dimensions. Aluminum adhesion may be enhanced with the addition of an underlying vapor deposited adhesion layer. A dielectric mask can be applied to pattern the aluminum surface into a plurality of electrodes prior to nanotube deposition.

The aluminum can also be pretreated to promote the adhesion of the carbon nanotubes. This can be done with any known pretreatments of aluminum. The carbon nanotubes can also adhere to other substrates, e.g.,  $\text{SnO}_2$ -in/Sb

### **The Electrophoresis Bath**

The electrophoretic deposition of the carbon nanotubes was conducted in an electrophoresis bath. The bath consists of a chamber to contain the solution of carbon nanotubes and means for immersing two opposing electrodes separated by some distance with the carbon nanotubes between the opposing electrodes. A DC power supply, external to the bath, is used to apply a voltage between the two electrodes immersed in the bath. The cathode lead is connected to the patterned aluminum substrate and the anode lead is connected to the other electrode. Tantalum was used for the second metal. The voltage applied to the two electrodes can be adjusted to a suitable level or the voltage can be adjusted to obtain a suitable current between the two electrodes.

The attachment of carbon nanotubes to the aluminum can be enhanced by a binder. The binders can be a mixture of Ag paste, carbon nanotubes and ethanol. Or the binders can be a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

### **Electrophoretic Deposition of Carbon Nanotubes on the Substrate**

A field emitter substrate is loaded into the electrophoresis bath. A plurality of cathodes are arranged on a glass substrate, and a dielectric film is formed with holes over the cathodes. Metal gates with openings which are located over the holes of the dielectric film are formed to expose the surface of the cathodes. Then, the carbon nanotubes are uniformly deposited onto the obtained substrate, on the surface of the cathodes exposed through the holes by electrophoretic deposition at room temperature.

### **Post Deposition Heat Treatment**

After the deposition of carbon nanotube particles by electrophoresis, low-temperature heating is performed to sustain the deposition of the carbon nanotubes on the cathodes and

ensure easy removal of impurities which are incorporated into the field emitter during the deposition.

### **EXAMPLE I**

#### **Preparation of Nanotube Film on Aluminum Substrate**

With reference to Figure 5, a solution is formed that contains 150 ml i-propyl alcohol (IPA) and 0.44 grams of acid washed carbon nanotubes. This solution is placed in an electrophoresis bath 5000.

A patterned, aluminum coated glass substrate 5002 serves as one electrode in electrophoresis bath 5000. The pattern forms the pixel size. The smallest feature size can be ca. 1 micron. The aluminum coated glass 5002 is about 55 mm x 45 mm x 1 mm in its dimensions. The aluminum pattern size is about 9 mm x 9 mm. The other electrode, tantalum (Ta) electrode 5004 is also inserted into the electrophoresis bath 5000. A spacer 5006 separates the aluminum coated glass 5002 from the tantalum electrode 5004. A DC voltage, for example between 40 to 120 volts, e.g., 100 volts is applied to the electrodes. A current between 1.0 to 5 mA, e.g., 3.8 mA, is observed between the electrodes. The duration of the preparation time can be between about 30 to about 90 minutes, e.g., 60 minutes.

Figure 6 illustrates an alternative electrophoretic method of creating the film according to the method disclosed in UK patent application 2,353,138 described below. First, a carbon nanotube suspension is created. The carbon nanotube particles can have lengths from about 0.1 to about 1  $\mu$ m. The suspension can also include a surfactant, e.g. an anionic, ionic, amphoteric or nonionic, or other surfactant known in the art. Examples of suitable surfactants include octoxynol, bis(1-ethylhexyl)sodium sulfosuccinate, and nitrates of  $\text{Mg}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  and  $\text{La}(\text{OH})_3$ .

The suspension is then sonicated to charge the carbon nanotube particles. The intensity of the electric field and the time for which the electric field is applied define the thickness of the carbon nanotube layer. Greater intensity and longer time yield thicker layers.

With reference to Figure 6 the field emitter substrate 6030 is loaded into the electrophoresis bath 6000 containing a carbon nanotube suspension 6010. An electrode plate 6020 is also installed in the electrophoresis bath 6000 spaced apart from the field emitter substrate 6030. The cathode of a DC power supply 6040, which is installed outside of the electrophoresis bath 6000, is connected to the other cathodes of the field emitter substrate 6030 and the anode of the DC power supply 6040 is connected to the electrode plate 6020. Then, a bias voltage of about 1 to about 1000 volts is applied from the DC power supply 6040 between the electrode plate 6020 and the cathodes of the field emitter substrate 6030.

As a positive voltage of the DC power supply 6040 is applied to the electrode plate 6020, carbon nanotube particles charged by positive ions in the carbon nanotube suspension 6010 migrate to and are attached to the exposed cathodes of the field emitter substrate 6030, which results in the formation of a carbon nanotube film in the pattern of the exposed cathodes.

The height of the printed carbon nanotube film, also known as the ink, coating, or paste, may be less than 10 microns and the space which isolates carbon nanotube cathodes from the indium tin oxide anode with indium tin oxide and phosphor is about 125 microns.

The electrophoresis process can be applied to both diodes and triodes. For applications to a diode, an electric field having opposite charges to those on the surfaces of the carbon nanotube particles is applied to exposed electrode surface of a field emitter substrate for selective deposition of carbon nanotube particles thereon. For application to a triode having gates, a weak positive electric field is applied to the gates while a positive electric field is applied to the

electrodes of the field emitter substrate, which avoids deposition of carbon nanotube particles on the gates. In particular, the electrode plate is connected to the anode of the DC power supply and the cathodes of the field emitter substrate are connected to the cathode of the DC power supply. As a positive potential is applied to the gates, the gates repel positive ions in the carbon nanotube suspension at the surface, while the exposed cathodes of the field emitter substrate, which are connected to the cathode of the DC power supply, pull positive ions of the suspension through the holes. As a result, the carbon nanotubes are deposited only on the entire exposed surface of the cathodes, not on the gates of the field emitter substrate. At this time, carbon nanotube particles are attracted to the field emitter substrate and are oriented substantially horizontal, or substantially parallel to the substrate, which allows the carbon nanotube particles to smoothly migrate through the holes to the cathodes, and thus the carbon nanotubes can be deposited.

The film can also be prepared similarly to the carbon ink disclosed in European Patent Application EP 1 020 888 A1 - *Carbon ink, electron-emitting element, method for manufacturing and electron-emitting element and image display device*

#### **Alternative Methods to Prepare Carbon Nanotube Films**

In addition to electrophoresis, other processes such as screen printing can be used for creating the patterns. A screen printing process is disclosed in U.S. Patent No. 6,270,369. In addition to screen printing, the carbon nanotubes can be applied to a substrate by ink jet printing. Ink printing is accomplished with carbon nanotube based liquid media or inks in which the fibrils are nearly individualized. Inks typically contain a carrier liquid and carbon nanotubes, and may be dried (i.e. evaporate the carrier liquid).

The carbon nanotubes can also be deposited in the form of a mat. Such porous mats, having densities between 0.10 and 0.40 gm/cc are conveniently formed by filtration of

suspensions of nanotubes as described in US Patents Nos. 6,099,965 and 6,031,711. Oxidized nanotubes are easily dispersed in and then filtered from aqueous media. The mats may be subjected to a rigidization or cross linking step as discussed in the aforecited patents.

Carbon nanotube mat cathodes have uniform emission sites at relatively low applied field and may obtain a current density of more than  $10 \text{ mA/cm}^2$ .

A comparison of the electron emission behavior of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats in the form of plots of current density as a function of the electric field is displayed in Figure 14. A further comparison of the electron emission patterns of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats is displayed in Figure 15.

#### **Carbon Nanotube Based Inks**

In yet another method, fibril based inks can be formulated for use in spray equipment. When combined with a masking technology, spray painting of fibril based inks offers a suitable method for depositing fibril ink patterns of either simple or complex designs. Spray painting can also be used to apply a uniform coating over a large area, with or without a masking technology. Spraying equipment can accommodate inks/paints with a wide range of viscosity and thixotropy. Airbrushes are a type of sprayer widely used in the graphic arts industry and areas where fine detailed spraying is desired.

The inks are sprayed through a stencil (i.e., mask, layer with cut out pattern, etc.) to form the corresponding pattern on the substrate and the carrier fluid is allowed to evaporate. The ratio of air to ink and the distance from the substrate can be adjusted to allow the optimum amount of drying of the aerosol droplets before they impinge on the substrate surface. In this way the adhesion of the droplets to the substrate and the tendency of the ink to run or spread can be



controlled. Once dried the dried ink can have conductivity approaching that of a bare fibril mat depending on the level of any binder that may have been included in the ink formulation.

The compositions are prepared by dispersing oxidized fibrils in water first, then adding other additional ingredients if so desired.

The formation of thin fibril films with these compositions can be achieved by both printing and dip coating. Text and patterns have been printed with an Epson® ribbon printer. The surface resistivity of printed pattern was measured about  $3.5 \times 10^5 \Omega\text{-cm}$  (sample 4 in Table 1). The thickness of the pattern is in the range of few tens of nanometers, corresponding few layers of fibrils. Papers with  $\sim 2.5\text{mm}$  fibril coating on both sides have been prepared by dip-coating method. Measured surface resistivity for the coated paper is between 200-300  $\Omega\text{-cm}$ . Bulk resistivity of the fibril coating is  $\sim 5 \times 10^{-2} \Omega\text{-cm}$ , a number very close to that measured for a freestanding fibril mat. Furthermore, adhesion of fibril films to the paper is excellent due to the strong interaction between functional groups on the fibril surface and groups associated with cellulose paper.

**Table 1.**

**Composition and Properties of Fibril-Based Ink**

| Sample | Composition(%) |                  |    |      |      | V(cps) | t( $\mu\text{m}$ ) | Resistivity                            |                           |
|--------|----------------|------------------|----|------|------|--------|--------------------|--|---------------------------|
|        | Fibril         | H <sub>2</sub> O | EG | SS   | DIOP |        |                    | $\rho_{\text{sur}} (\Omega\text{-cm})$ | $\rho (\Omega\text{-cm})$ |
| 1      | 2              | 98               | —  | —    | —    | 0      | 2.5                | 200-300                                | $5 \times 10^{-2}$        |
| 2      | 4              | 96               | —  | —    | —    | 19.2   | —                  | —                                      | —                         |
| 3      | 2.5            | 77.5             | 20 | —    | —    | 0      | —                  | —                                      | —                         |
| 4      | 2.5            | 77.17            | 20 | 0.03 | 0.3  | 0      | —                  | $3.5 \times 10^5$                      | $5 \times 10^{-2}$        |

### **Modification of Carbon Nanotube Films**

The carbon nanotubes, or film, may be modified by chemical or mechanical treatment. The surface may be treated to introduce functional groups. Techniques that may be used include exposing the carbon nanotubes to electromagnetic radiation, ionizing radiation, plasmas or chemical reagents such as oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, and strong bases and /or combinations thereof. Of particular interest is plasma treatment.

### **Plasma Treatment of Nanotube Films**

Plasma treatment is carried out in order to alter the surface characteristics of the carbon fibrils, fibril structures and/or the matrix, which come in contact with the plasma during treatment; by this means the fibril composite treated can be functionalized or otherwise altered as desired. Once equipped with the teaching herein, one of ordinary skill in the art will be able to adapt and utilize well-known plasma treatment technology to the treatment of such composite materials. Thus, the treatment can be carried out in a suitable reaction vessel at suitable pressures and other conditions and for suitable duration, to generate the plasma, contact it with the composite material, and effect the desired kind and degree of modification. Plasmas such as those based on oxygen, hydrogen, ammonia, helium, or other chemically active or inert gases can be utilized.

Examples of other gases used to generate plasmas include, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfurhexafluoride, perfluoroethylene, fluoroform, difluorodichloromethane, bromo-trifluoromethane, chlorotrifluoromethane, and the like. Plasmas may be generated from a single gas or a mixture of two or more gases. It may be advantageous to expose a composite material to more than one type of plasma. It may also be advantageous to expose a composite material to a plasma multiple times in succession; the conditions used to

generate the plasma, the duration of such successive treatments and the duration of time between such successive treatments can also be varied to accomplish certain alterations in the material. It is also possible to treat the composite material, e.g., coat the material with a substance, wash the surface of the material, etc., between successive treatments.

Plasma treatment of a composite material may effect several changes. For example, a composite material comprising a polymer and a plurality of carbon fibrils dispersed therein can be exposed to plasma. Exposure to plasma may etch the polymer and expose carbon fibrils at the surface of the composite, thus increasing the surface area of exposed carbon fibrils, e.g., so that the surface area of the exposed fibrils is greater than the geometric surface area of the composite. Exposure to plasma may introduce chemical functional groups on the fibrils or the polymer.

Treatment can be carried out on individual fibrils as well as on fibril structures such as aggregates, mats, hard porous fibril structures, and even previously functionalized fibrils or fibril structures. Surface modification of fibrils can be accomplished by a wide variety of plasmas, including those based on  $F_2$ ,  $O_2$ ,  $NH_3$ , He,  $N_2$  and  $H_2$ , other chemically active or inert gases, other combinations of one or more reactive and one or more inert gases or gases capable of plasma-induced polymerization such as methane, ethane or acetylene. Moreover, plasma treatment accomplishes this surface modification in a "dry" process as compared to conventional "wet" chemical techniques involving solutions, washing, evaporation, etc. For instance, it may be possible to conduct plasma treatment on fibrils dispersed in a gaseous environment.

Once equipped with the teachings herein, one of ordinary skill in the art will be able to practice the invention utilizing well-known plasma technology. The type of plasma used and length of time plasma is contacted with fibrils will vary depending upon the result sought. For instance, if oxidation of the fibrils' surface is sought, an  $O_2$  plasma would be used, whereas an

ammonia plasma would be employed to introduce nitrogen-containing functional groups into fibril surfaces. Once in possession of the teachings herein, one skilled in the art would be able to select treatment times to effect the degree of alteration/functionalization desired.

More specifically, fibrils or fibril structures are plasma treated by placing the fibrils into a reaction vessel capable of containing plasmas. A plasma can, for instance, be generated by (1) lowering the pressure of the selected gas or gaseous mixture within the vessel to, for instance, 100 - 500 mTorr, and (2) exposing the low-pressure gas to a radio frequency which causes the plasma to form. Upon generation, the plasma is allowed to remain in contact with the fibrils or fibril structures for a predetermined period of time, typically in the range of approximately 10 minutes more or less depending on, for instance, sample size, reactor geometry, reactor power and/or plasma type, resulting in functionalized or otherwise surface-modified fibrils or fibril structures. Surface modifications can include preparation for subsequent functionalization.

Treatment of a carbon fibril or carbon fibril structure as indicated above results in a product having a modified surface and thus altered surface characteristics which are highly advantageous. The modifications can be a functionalization of the fibril or fibril structure such as chlorination, fluorination, etc., or a modification which makes the surface material receptive to subsequent functionalization, optionally by another technique or other chemical or physical modification as desired.

#### **Chemical Treatments of Nanotube Films**

Chemical treatment can be also used. Acid treatments, particularly severe acids treatments, result in cutting the lengths of nanotubes, sharpening the ends of nanotubes, creating defects on the surface of nanotubes and introducing functional groups on the surface of nanotubes. Acid treated nanotubes are water dispersible, so chemical treatment offers advantages

for the formation of nanotube film electrodes. Functional groups can be mostly removed by thermal treatment. The process for doing this is disclosed in U.S. Patent No. 6,203,814. The Raman effect or titration can be used to measure the effect of the acid treatment. Raman can be used to measure the degree of structure imperfection after removing oxygen groups introduced during acid treatment. The effect of the treatment can be measured by electron spin resonance or simple titration as disclosed therein. See also, R. Khan et al. *Electron Delocalization in Amorphous Carbon by Ion Implantation*, 63 PHYSICAL REVIEW B 121201-1 (2001).

In metal vapor treatment procedures metal atoms can be introduced into nanotube films by heating films under vapor of a metal. For example, Cs atoms, which have been shown to enhance field emission, can be introduced into a nanotube film by placing the film in a vacuum chamber which has a Cs source held at 200 °C above (Vapor pressure of Cs at 373 °C is 10 mm Hg).

Chemical vapor transport methods can be used. Most metals vaporize at very high temperature. Metal atoms of these metals, such as Ga, can be introduced into nanotube films by chemical vapor transport. The nanotube film is placed in an evacuated glass tube, at one end. a metal particle is placed at the other end. A chemical vapor transport agent, such as Cl<sub>2</sub>, I<sub>2</sub>, Br<sub>2</sub> and HCl is also included. The tube is placed into a three-zone furnace. The temperature of nanotube is held lower than that of the metal, so that metal atoms are transported to the nanotube films by the transport agent.

Chemical sorption followed by heat treatment can be used. Metal atoms can be introduced into nanotube films by first absorbing a metal compound like metal halides or organometallic compounds on the surface of the nanotube films, followed by heating then under inert gas atmosphere to convert metal halides or organometallic compounds to metal atoms. For

example Ge atoms may be introduced into a nanotube film by absorbing  $\text{GeBr}_2$  on the surface of nanotubes from a  $\text{GeBr}_2$  alcohol solution, then heating the nanotube film between 200 and 400 °C to decompose  $\text{GeBr}_2$ .

Functionalization of nanotubes by chemical sorption can be used, some molecules, like metal phthalocyanines may have the effect of lowering work function of nanotubes and lead to an enhancement of field emission when absorbed on the surface of nanotubes. Absorption can be carried out by placing a nanotube film electrode in a phthalocyanine, porphyrin or metalloporphyrin solution; this procedure is disclosed in U.S. Patent No. 6,203,814. The functionalization is carried out by phthalocyanines, metalloporphyrins, porphyrins or other organometallics.

The treatment can also include annealing the film after functionalization. The annealing temperature can be carried out between 200 and 900 degrees Celsius in inert gas or under 360 degrees Celsius in air.

#### **Ion Bombardment of Carbon Nanotube Films**

The carbon nanotube films, are treated by ion bombardment before use in a field emission device or field emitting cathode.

The settings used to bombard the carbon nanotubes were as follows:

energy: 30 keV. Other ranges appropriate for the present invention can be from about 5eV to about 1MeV, e.g., 10-50 keV.

ion: Ga. Although Ga was used as the ion, any type of ion can be used. Other types of ions, for example, include H, He, Ar, C, O, and Xe.

spot size: defocused, 500 nm. Other ranges appropriate for the present invention include from about 1 nm to about 1 micron. Appropriate spot size can also be based on desired resolution and dose.

scan area: 760 microns x 946 microns Rasterscanned for about twenty seconds. Any appropriate scan area will suffice.

dose:  $2 \times 10^{14} / \text{cm}^2$  ranges include from about  $10^2 / \text{cm}^2$  to about  $10^{20} / \text{cm}^2$

#### **Additional Methods for Treatments of Nanotube Films**

Other energetic beams/sources, including atomic beams, electron beams, neutron beams, molecular beams, lasers, plasmas, UV light, x-ray and gamma rays can be used to treat nanotube films instead of ion bombardment. Mechanical treatment resulting in mechanical disruption, for example, ball milling can be used.

Other characteristics of carbon nanotubes can be modified by the above treatments. For example, the treatments can remove surface oxygen, remove insulating oxidation residues, generate edges, points, and singularities, recrystallize the tubes, generate non-tube carbon nanoparticles. A treatment can also be used to clean the carbon nanotubes, for example cleaning to remove the insulation coating generated by oxidation and cleaning to remove oxygen.

#### **Characterization of the Treated Film**

By viewing samples in a SEM it is possible to detect irradiated areas by contrast change, i.e., dark image. Figure 12 illustrates scanning electron microscope views of carbon nanotubes on aluminum.

Figure 7 schematically illustrates an apparatus used to make the emission measurements. Figure 7 illustrates the top view, Figure 7a, and side views, Figure 7b. Figure 7a shows a 6 mm x 6 mm phosphor on indium tin oxide (ITO). In Figure 7b, the phosphor is shown to be spaced

from the patterned carbon nanotubes by a distance of 125  $\mu\text{m}$ . The entire system is evacuated with a vacuum of  $5 \times 10^{-9}$  Torr in the emission chamber.

The degree of improvement achieved by ion beam treatment are summarized in Table 2.

**Table 2**

|                   | Untreated CNT Cathode | Treated / Modified CNT Cathode |
|-------------------|-----------------------|--------------------------------|
| Threshold voltage | 350 Volts             | 140 Volts                      |
| Threshold Field   | 2.8 V / $\mu\text{m}$ | 1.1 V / $\mu\text{m}$          |
| Emission current  | see figure 8          | 6 times increase               |

The ion bombardment achieves a reduction in work voltage, increases emission current and increases the number of emission sites. With reference to Figure 8, it is seen that the turn-on voltage was reduced substantially as the result of ion beam treatment.

Figure 9 is a Fowler-Nordheim (F-N) plot. The shape of the curves provides the theoretical proof of FE. Shifting the curve toward the right side - toward lower voltage - indicates an increased number of emission sites.

Similar improvements can be obtained by treating the carbon nanotubes with ultra-violet light, laser beam and plasma.

## **EXAMPLE II**

### **Emission Characteristics of Ion-Beam-Treated Nanotube Films**

Carbon nanotube films fabricated by electrophoresis on an aluminum layer deposited on a glass have been locally irradiated with focused ion beams. A diode structure with a distance of 125  $\mu\text{m}$  between cathodes and anodes was used for emission measurement. A maximum emission current of 375 microamps with a turn-on voltage of 2.8 V/ $\mu\text{m}$  for carbon nanotube



emitters was found to decrease by focused ion beam irradiation to 1.1 V /  $\mu\text{m}$  with increase in emission current by a factor of six.

The current range that was used in the test was in the low range with an anode voltage of about 400 to 500 volts, close to the turn-on (threshold) voltage for field emission. The change was from 0.05 to about 0.18 microamps to more than 0.9 microamps with a drastic change in the F-N plot of Figure 9.

The physical and chemical effects of ion bombardment on carbon nanotubes are not entirely known. While not wishing to be bound to any particular theory, it may be that the effect of the ion bombardment is the creation of surface sites which enhance field emission. It is believed that the treatment 1) cuts lengths of nanotubes, in particular, if high energy beams are used, hence generating more ends; 2) implants ions, like Ga ions, into the nanotube film, the ions being inside a single tube and outside tubes; 3) saturates dangling bonds with hydrogen (where a hydrogen ion beam/plasma is used), resulting in hydrogenated surface; 4) cleans the surface of nanotubes by removing contaminants, such as binder residue and oxygenated groups; 5) generates localized and delocalized regions along the nanotube axis by creating pits and carbon nanoparticles and recrystallizing amorphous carbons on the surface of nanotubes, and disrupting carbon layers, leading to an increasing in emission sites; 6) improves electric contacts between nanotubes.

The surface sites generated by ion bombardment can be defects, which are carbon atoms at edges, carbon atoms associated with other atoms, like a hydrogen atom, and an implanted Ga atom, and carbon atoms with a  $\text{sp}^3$  configuration or configurations between  $\text{sp}^2$  and  $\text{sp}^3$ . The defects can be at the ends (exposed) of a nanotube, and on the surface of a single nanotube associated with a nanoparticle, a pit and a disrupted carbon layer.

### **Construction of a Field Emission Display Device Using Treated Carbon Nanotube Cathodes**

Generally, field emission display devices are based on the emission of electrons in a vacuum. Emitter tips emit electrons that are accelerated in a strong electric field. The electrons ultimately collide with fluorescent materials that emit light. The advantages of this type of display over other types, such as cathode ray tubes, are that they are very thin and light and yield high brightness and resolution. Processes for constructing these devices are disclosed in EP No. 1,073,090 A2.

Figure 1 shows an exemplary embodiment of a field emission display device using an treated carbon nanotube cathode. The field emission display 1000 includes, for example, a first substrate 1010, first metal film 1020, a conductive high polymer film 1030, a dielectric film 1040, a second metal film 1050, a spacer 1060, a transparent electrode 1070, a second substrate 1080, and emitter tips, the treated carbon nanotube cathode, 1090.

The substrate 1010 is, for example, made of glass quartz, silicon, or alumina ( $\text{Al}_2\text{O}_3$ ). Other substrates include silica, platinum, iron and its alloys, cobalt and its alloys, nickel and its alloys, and ceramics.

The first metal film 1020 functions as the cathode and is, for example, made of chrome, titanium, tungsten, or aluminum. The first metal film 1020 has a thickness from about 0.2 to about 0.5  $\mu\text{m}$ .

On the first metal film 1020 is, for example, the dielectric film 1040. The dielectric film 1040 has a thickness from about one to about five  $\mu\text{m}$ .

On the dielectric film 1040 is the second metal film 1050. The second metal film 1050 functions as a gate electrode and is made from, for example, chrome, titanium, or palladium. The thickness of the second metal film is from about 0.2 to 0.5  $\mu\text{m}$ . The second metal film 1050

can also be patterned, for example, by using a photoresist film that has a thickness from about 1.5 to about 2.0  $\mu\text{m}$ . The photoresist film is later developed forming a photoresist pattern. The accelerating gate electrode should be in close proximity to the emitting source approximately one to ten  $\mu\text{m}$ .

Both the first metal film 1020 and the dielectric film 1040 have a plurality of fine holes. The holes have, for example, a diameter of 0.5 to 10.0  $\mu\text{m}$  and are separated from each other by about 2.0 to about 15.0  $\mu\text{m}$ .

Formed within the fine holes of the dielectric film 1040 and the second film 1050, is the conductive high polymer film 1030. The conductive high polymer film 1030 can be, for example, made from carbon adhesive or silver adhesive. To attach the conductive high polymer film 1030 to the first metal film 1020, the conductive high polymer film 1030 is liquefied by heating and poured to fill approximately one-third of each of the fine holes.

Arranged vertically or horizontally within the conductive high polymer film 1030 are carbon nanotubes used as emitter tips 1090. The emitter tips 1090 are made from the ion bombarded carbon nanotubes discussed previously. These emitter tips 1090 can obtain a great amount of emission current at a low operating voltage, for example, about 1.5 V/ $\mu\text{m}$ . The range can be from about 0.1 to about 2.0 V/ $\mu\text{m}$ , e.g., about 0.8 V/ $\mu\text{m}$  to about 1.5V/ $\mu\text{m}$ .

Above the second metal film 1050 is the spacer 1060. The spacer 1060 is installed to about 100 to about 700  $\mu\text{m}$ . on the second metal film 1050.

The transparent electrode 1070 is on top of the spacer 1060. The transparent electrode 1060 functions as an anode and is made of a conducting oxide, such as indium oxide, indium tin oxide, tin oxide, copper oxide, or zinc oxide.

The second substrate 1080 is on the transparent electrode 1070 and can be made of glass. Fluorescent material, attached to the transparent electrode 1070, emits red, blue, or green light when electrons contact it.

The emitter tips 1090 are made of the ion bombarded carbon nanotubes. The geometrical features of the emitter tips 1090 should be small. For example, the diameters of each emitter tip 1090 should be as small as 1.3 nm. The average height of the nanotubes is from about 0.1 to about 1000  $\mu\text{m}$ , preferably between 0.1 to about 100  $\mu\text{m}$ . The average diameter is between 1.3 to 200 nm depending on whether the nanotubes are single walled or multi-walled.

More than  $10^4$  emitting tips are needed per pixel of  $100 \times 100 \mu\text{m}^2$  assuming 50% of nanotube density with a tubule diameter of about 10 to about 100 nanometers. The emitter density is preferably at  $1 / \mu\text{m}^2$ , in particularly at least  $10 / \mu\text{m}^2$ . The entire field emission display 1000 is evacuated.

In Figure 2, a field emission display 2000 is shown. The field emission display 2000, includes, for example, a baseplate 2010, a spaced-apart phosphor coated faceplate 2020, and an electron emitter array 2030 positioned on the baseplate 2010 for emitting electrons that collide with the phosphor causing illumination. The components of the field emission display 2000 are in a vacuum. The electron emitter array (cathode) 2030 is composed of treated carbon nanotubes that can have either an orientation parallel, perpendicular, or any angle between zero and ninety degrees to the baseplate 2010. (See PCT/US 99/13648 - Free Standing and Aligned Carbon Nanotubes and Synthesis thereof).

Figure 3 shows yet another embodiment of the field emission device. The device 3000, has, for example, a substrate 3010, a porous top layer 3020, a catalyst material 3030, and bundles of treated carbon nanotubes 3040 as the cathode.

The substrate 3010 and the porous top layer 3020 can be made of, for example, silicon. The catalyst material 3030 can be a thin film of iron oxide that is formed in a particular pattern. The carbon nanotube bundles 3040 serve as the cathode. The bundles 3040 are oriented substantially perpendicular to the substrate 3010. Alternatively, the bundles 3040 can also be oriented substantially parallel to the substrate 3010.

The carbon nanotube bundles 3040 may be about 10-250  $\mu\text{m}$  wide, and up to or greater than three hundred  $\mu\text{m}$  in height. The bundles 3040 are of the same size and shape as the patterns of catalyst material 3030, for example. The nanotube bundles 3040 can have flat tops or bowl-shaped tops as shown in the figure. The sharp edges of the nanotube bundles 3040 function as field emission regions. Each bundle 3040 provides the field emission for a single pixel in a flat panel display.

The device is evacuated to from about  $10^{-3}$  Torr to about  $10^{-9}$  Torr, e.g., from about  $10^{-7}$  Torr to about  $10^{-8}$  Torr.

The calculation of any electrical field within the device 3000 is made by taking the applied voltage and dividing it by the distance from the emitter tips to the anode. See (PCT appln. PCT/US99/26332)

Figure 4 shows another embodiment of a flat panel field emission display 4000. The display 4000, for example, includes cathode 4010 that contains a plurality of treated carbon nanotube emitting tips 4020 and an anode 4030. The anode 4030 further includes an anode conductor 4040 and a phosphor layer 4050. Between the cathode 4010 and the anode 4030 is a perforated conductive gate electrode 4060. Between the gate electrode 4060 and the cathode 4010 is an insulating layer 4070. The space between the anode 4030 and the carbon nanotube emitting tips are sealed and evacuated. The voltage is supplied by a power supply. The

electrons emitted from the emitting tips 4020 are accelerated by the gate electrode 4060, and move toward the anode conductor layer 4080 which is a transparent conductor such as indium-tin oxide. The gate electrode 4060 should be within 10  $\mu\text{m}$  of the emitting tips 4020. As the emitted electrons hit the phosphor layer 4050, light is given off. (see, EP 1,022,763 A1). The colors of the emitted light depend on the phosphors that are used. For example Zn:Scu, Al for green,  $\text{Y}_2\text{O}_3\text{:Eu}$  for Red, and ZnS:Ag for blue.

The cathodes and anodes can be referred to as sources and drains respectively.

### **Operation of a Field Emission Device**

To operate the field emission display device, the treated carbon nanotube cathode is held at a negative potential relative to the anode. As a result of this potential difference, electrons are emitted from the emitter tips and travel to the anode. The gate electrode can be used to accelerate the emitted electrons.

### **Field Emission Display Devices**

Using the ion bombarded carbon nanotube cathode, various devices can be created, such as a field emitter array. An array can include a single nanotube, a single bundle, or many carbon nanotubes and field emission display, e.g., a flat panel television. The treated carbon nanotube can constitute the array. Figure 10 is an illustration of a classical field emitter.

Table 3 shows example characteristics of a field emitter display

**Table 3**

| emission type                  | low & high voltage |
|--------------------------------|--------------------|
| brightness ( $\text{cd/m}^2$ ) | 150, 600           |
| viewing angle (degrees)        | 160                |
| emission efficiency (lm)       | 10-15              |
| response time                  | 10-30              |
| contrast ratio                 | > 100:1            |
| number of colors               | 16 million         |
| number of pixels               | 640/480            |

|                           |          |
|---------------------------|----------|
| resolution (mm pitch)     | 0.31     |
| power consumption (W)     | 2        |
| max screen size (cm)      | 26.4     |
| panel thickness (mm)      | 10       |
| operating temp range (°C) | -5 to 85 |

The advantages of field emission display over other types of displays such as cathode ray tubes include: high brightness, peak brightness, full viewing angle, high emission efficiency, high dynamic range, fast response time and low power consumption.

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#### *Other Uses*

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We claim:

1. A field emission device comprising:

a cathode; and

an anode spaced from the cathode,

wherein said cathode includes emitters comprising carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment.

2. The field emission device of claim 1, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layers concentric with their cylindrical axes, said carbon fibrils being substantially free of pyrolytically deposited carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

3. The field emission device of claim 1, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates.

4. The field emission device of claim 1, wherein said nanotubes have a morphology resembling a fishbone.

5. The field emission device of claim 1, wherein said nanotubes are single wall nanotubes.

6. The field emission device of claim 1, wherein said nanotubes are in the form of a film or mat.

7. The field emission device of claim 1, wherein said nanotubes have been treated with an ion beam.

8. The field emission device of claim 1, wherein said nanotubes have been treated with a gallium ion beam.

9. The field emission device of claim 1, wherein said nanotubes have been treated with a beam of ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

10. The field emission device of claim 1, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport and chemical sorption.

11. The field emission device of claim 1, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

12. The field emission device of claim 1, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

13. The field emission device of claim 1 wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

14. The field emission device of claim 1 wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

15. The field emission device of claim 1, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

16. The field emission device of claim 1, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

17. The field emission device of claim 16, wherein said functional groups have been introduced by chemical sorption.

18. The field emission device of claim 1, wherein said treatment comprises heating the carbon nanotubes in the presence of metal vapor.

19. The field emission device of claim 1, wherein said treatment comprises chemisorption followed by heat treatment.

20. The field emission device of claim 1, wherein said treatment includes annealing said nanotubes.

21. The field emission device of claim 1, wherein said cathode further includes a binder.

22. The field emission device of claim 21, wherein said binder is a conductive carbon paste, conductive metal paste or carbonizable polymer.

23. A process for treating carbon nanotubes comprising the step of bombarding carbon nanotubes with ions.

24. The process for treating carbon nanotubes of claim 23, wherein the nanotubes are bombarded with gallium ions.

25. The process of treating carbon nanotubes of claim 23, wherein the nanotubes are bombarded with ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

26. Carbon nanotubes formed by the process of claim 23.

27. A field emission cathode comprising carbon nanotubes, wherein said nanotubes have been subjected to energy, plasma, chemical, or mechanical treatment.

28. The field emission cathode of claim 27, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layers concentric with their cylindrical

axes, said carbon fibrils being substantially free of pyrolytically deposited carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

29. The field emission cathode of claim 27, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates or bird nest aggregates.

30. The field emission cathode of claim 27, wherein said nanotubes have a morphology resembling a fishbone.

31. The field emission cathode of claim 27 wherein said nanotubes are single wall nanotubes.

32. The field emission cathode of claim 27, wherein said nanotubes are in the form of a film or mat.

33. The field emission cathode of claim 27, wherein said nanotubes have been treated with an ion beam.

34. The field emission cathode of claim 27, wherein said nanotubes have been treated with a gallium ion beam.

35. The field emission cathode of claim 27, wherein said nanotubes have been treated with a beam of ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

36. The field emission cathode of claim 27, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

37. The field emission cathode of claim 27, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

38. The field emission cathode of claim 27, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

39. The field emission cathode of claim 27, wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

40. The field emission cathode of claim 27, wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

41. The field emission cathode of claim 27, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

42. The field emission cathode of claim 27, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

43. The field emission cathode of claim 42, wherein said functional groups have been introduced by chemical sorption.

44. The field emission cathode of claim 27, wherein said treatment comprises heating the carbon nanotubes in the presence of metal vapor.

45. The field emission cathode of claim 27, wherein said treatment comprises chemisorption followed by heat treatment.

46. The field emission cathode of claim 27, wherein said treatment includes annealing said nanotubes.

47. The field emission cathode of claim 27, wherein said cathode further includes a binder.

48. The field emission cathode of claim 47, wherein said binder is a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

49. The field emission cathode of claim 27, wherein the nanotubes are deposited onto a substrate.

50. A method for making a field emission cathode comprising the steps of:

dispersing carbon nanotubes into a liquid vehicle to form a solution;

forming an electrophoresis bath, said bath including an anode and a cathode immersed therein;

applying a voltage to said anode and said cathode, thereby causing said carbon nanotubes to deposit onto said cathode;

removing said cathode from said bath; and

subjecting the nanotubes deposited on said cathode to an energy, plasma, chemical, or mechanical treatment.

51. The method for making a field emission cathode of claim 50, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layer concentric with their cylindrical axes, said carbon fibrils being substantially free of pyrolytically deposited



carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

52. The method for making a field emission cathode of claim 50, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates or bird nest aggregates.

53. The field emission display device of claim 50, wherein said nanotubes have a morphology resembling a fishbone.

54. The method of making a field emission cathode of claim 50, wherein said nanotubes are single wall nanotubes.

55. The method of making a field emission cathode of claim 50, wherein said nanotubes are in the form of a film or mat.

56. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with ions.

57. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with a gallium ions.

58. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

59. The method for making a field emission cathode of claim 50, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

60. The method for making a field emission cathode of claim 50, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing

agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

61. The method for making a field emission cathode of claim 50, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

62. The method for making a field emission cathode of claim 50, wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

63. The method for making a field emission cathode of claim 50, wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

64. The method for making a field emission cathode of claim 50, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

65. The method for making a field emission cathode of claim 50, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

66. The method for making a field emission cathode of claim 65, wherein said functional groups have been introduced by chemical sorption.

67. The method for making a field emission cathode of claim 50, wherein said treatment comprises heating said cathode in the presence of metal vapor.

68. The method for making a field emission cathode of claim 50, wherein said treatment comprises chemisorption followed by heat treatment.

69. The method for making a field emission cathode of claim 50, wherein said treatment includes annealing said nanotubes.

70. The method for making a field emission cathode of claim 50, further comprising the step of adding a binder to said solution before applying said voltage.

71. The method for making a field emission cathode of claim 70, wherein said binder is a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

72. A field emission display device comprising:

- a cathode including carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment;
- an insulating layer on said cathode;
- a gate electrode on said insulating layer;
- an anode spaced from said cathode, said anode comprising a phosphor layer, an anode conducting layer, and a transparent insulating substrate; and
- a power supply.

73. A method for making a field emission cathode comprising the steps of:

- screen printing an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes in as-made form or which have been subjected to energy, plasma, chemical, or mechanical treatment; and
- evaporating said carrier liquid.

74. A method for making a field emission cathode comprising the steps of:

- ink jet printing an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes which have been in as-made form or which have been subjected to energy, plasma, chemical, or mechanical treatment; and

evaporating said carrier liquid.

75. A method for making a field emission cathode comprising the steps of:

spray painting an ink through a stencil onto a substrate, said ink comprising a carrier liquid and carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment; and

evaporating said carrier liquid.

76. A method for making a field emission cathode comprising the steps of:

screen printing, ink-jet printing or spray painting an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes in as-made form; and subjecting said screen printed nanotubes to an energy, plasma, chemical or mechanical treatment.

77. A field emission cathode made by the method of claim 107.

78. A field emission display device comprising:

a baseplate;

an electron emitter array, said array including carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment;

a gate on said baseplate;

a phosphor coated faceplate spaced from said gate;

a faceplate on said phosphor coated faceplate; and

a power supply.

79. A field emission device comprising:

a substrate,

a porous top layer on said substrate,

a catalyst material on said layer; and

a cathode on said catalyst material, said cathode including a bundle of carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment.

# FIELD EMISSION DISPLAY (1000)

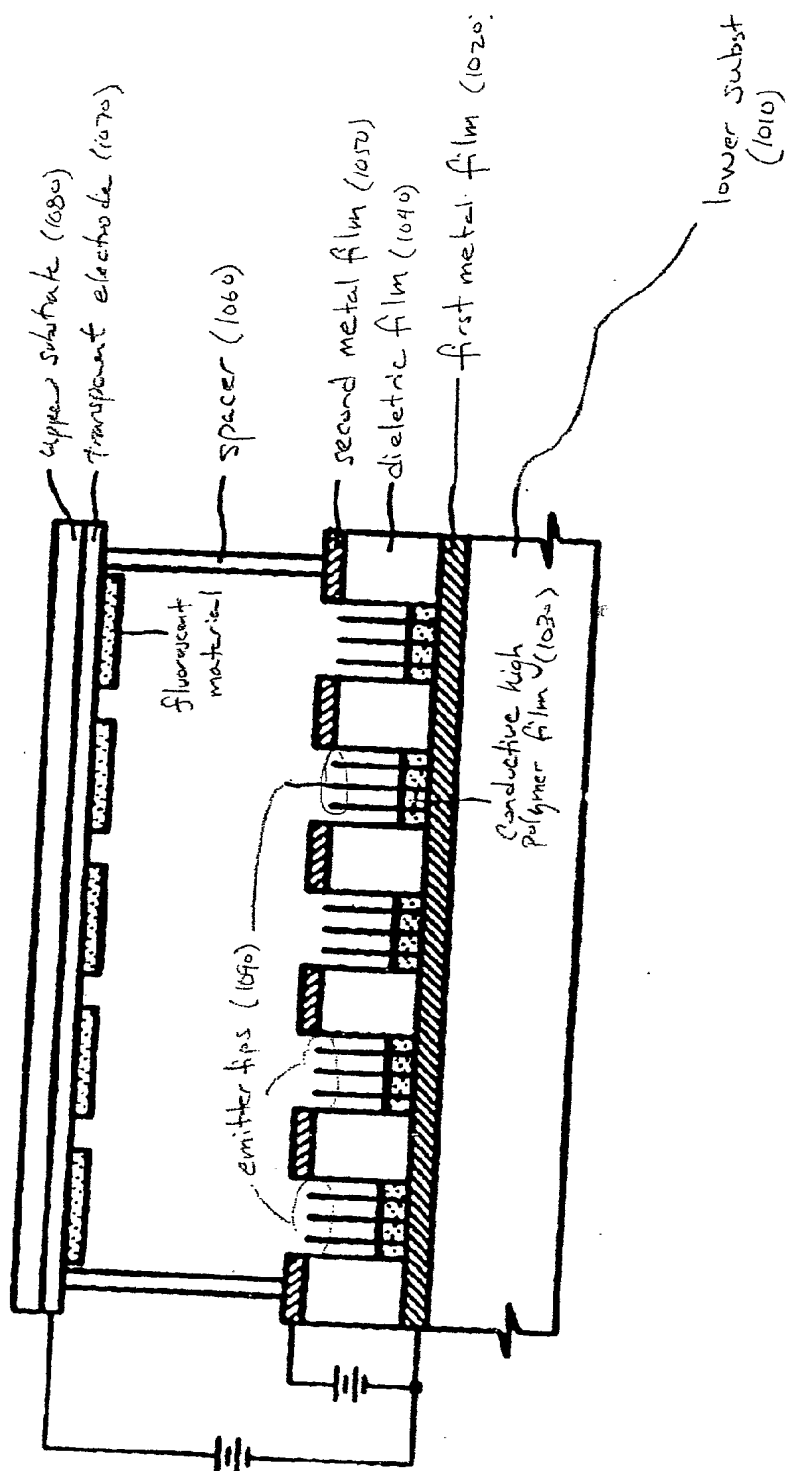


Fig. 1

FIG. 2

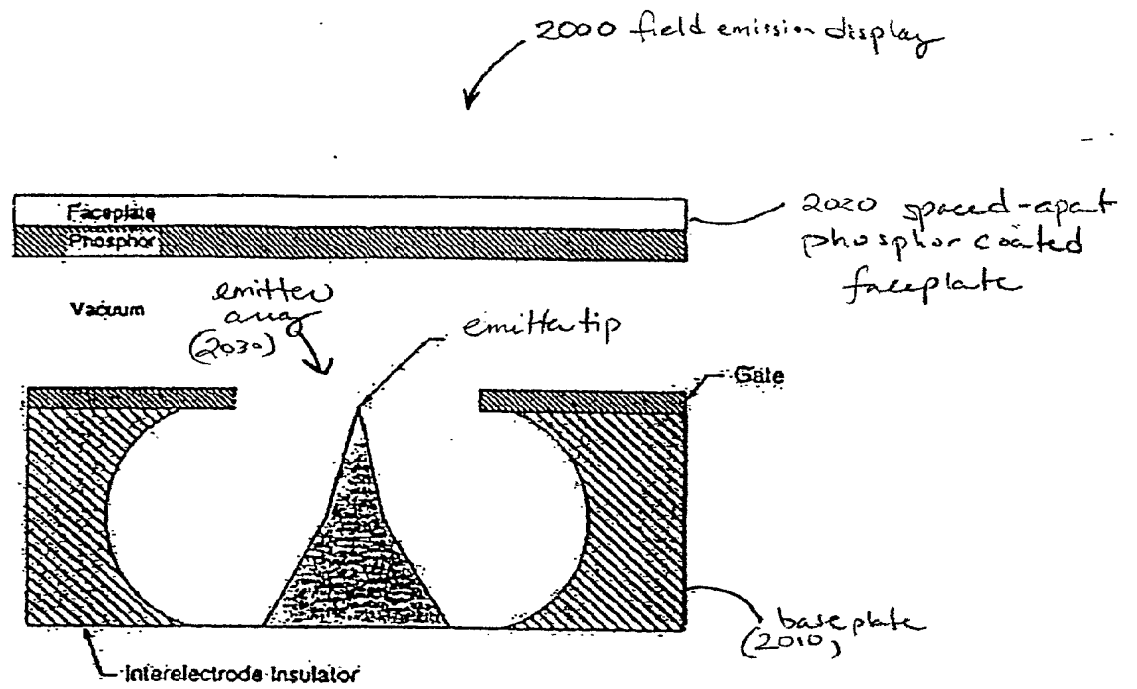
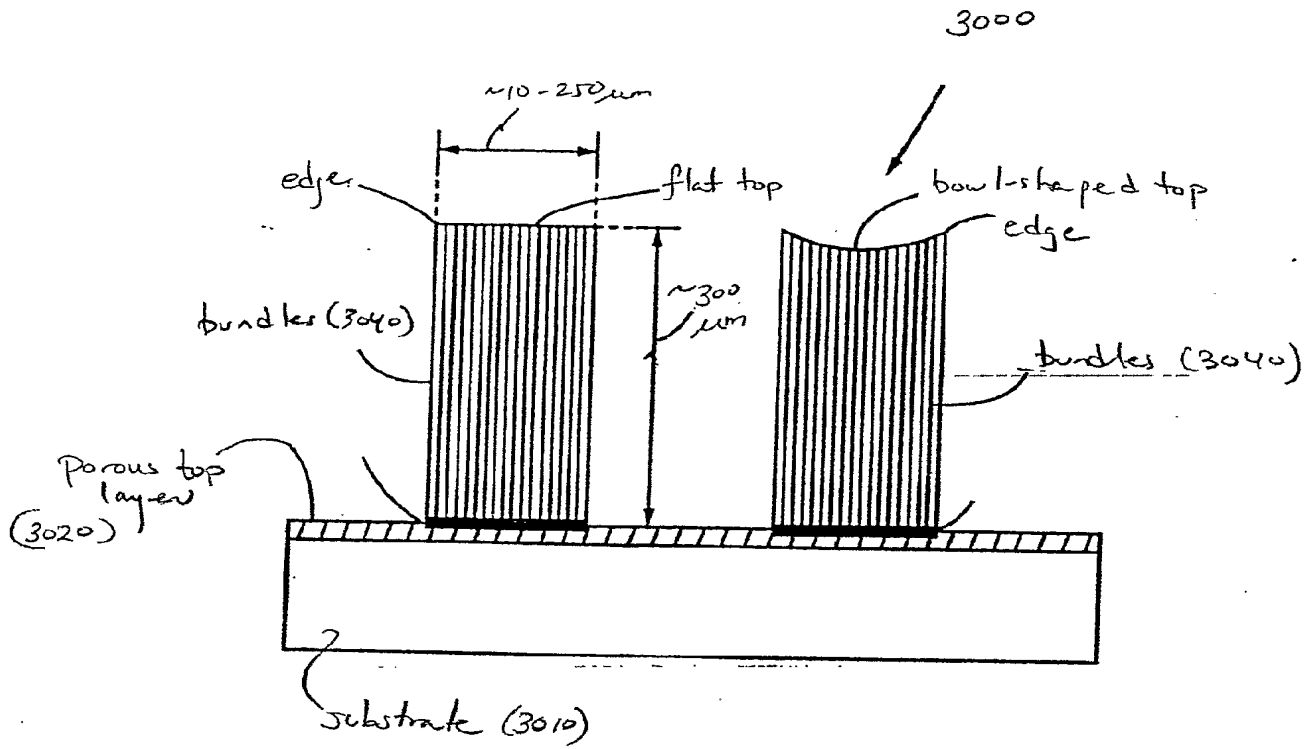


Fig. 3



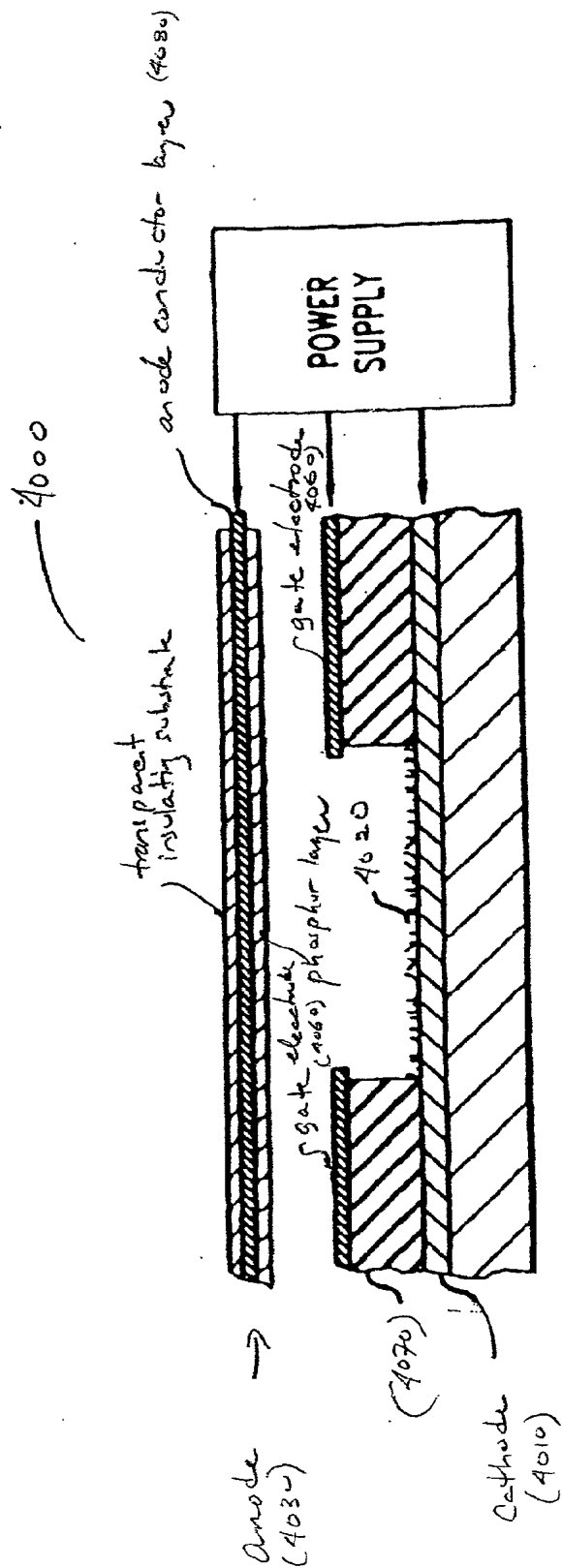


Fig 4

Fig 5

# Electro Phoresis / Deposition

Solution

CNT 0.44 g

IPA 150 ml

Electrode

Al (9 mm x 9 mm) x 3

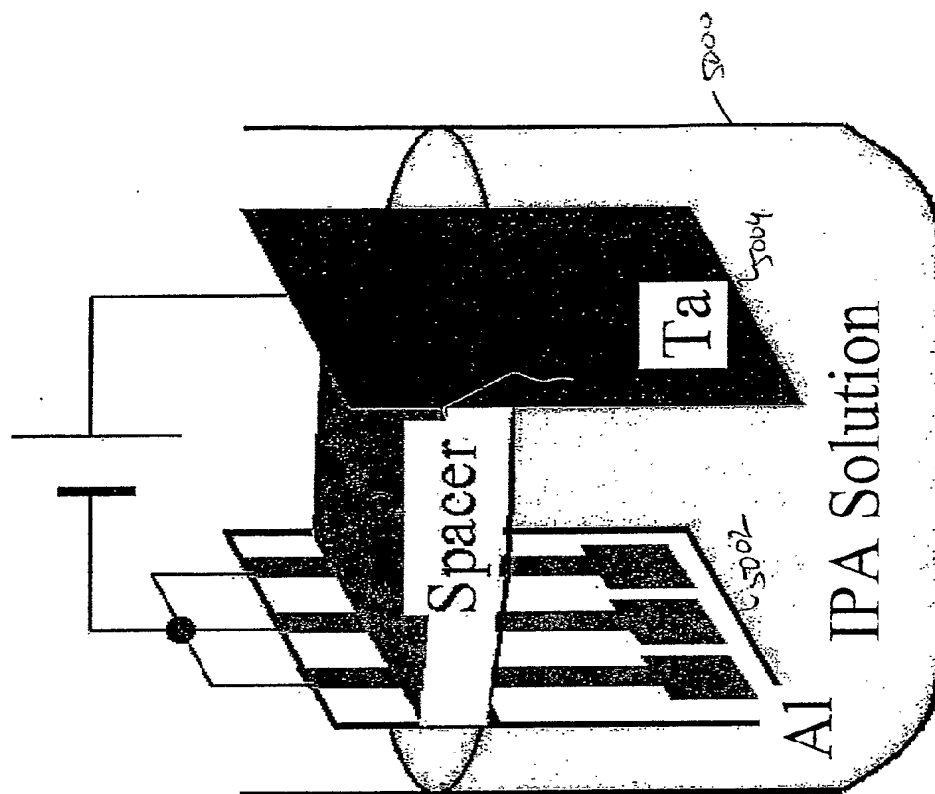
Voltage

DC 100 V

Current

3.8 mA

Time 30 min

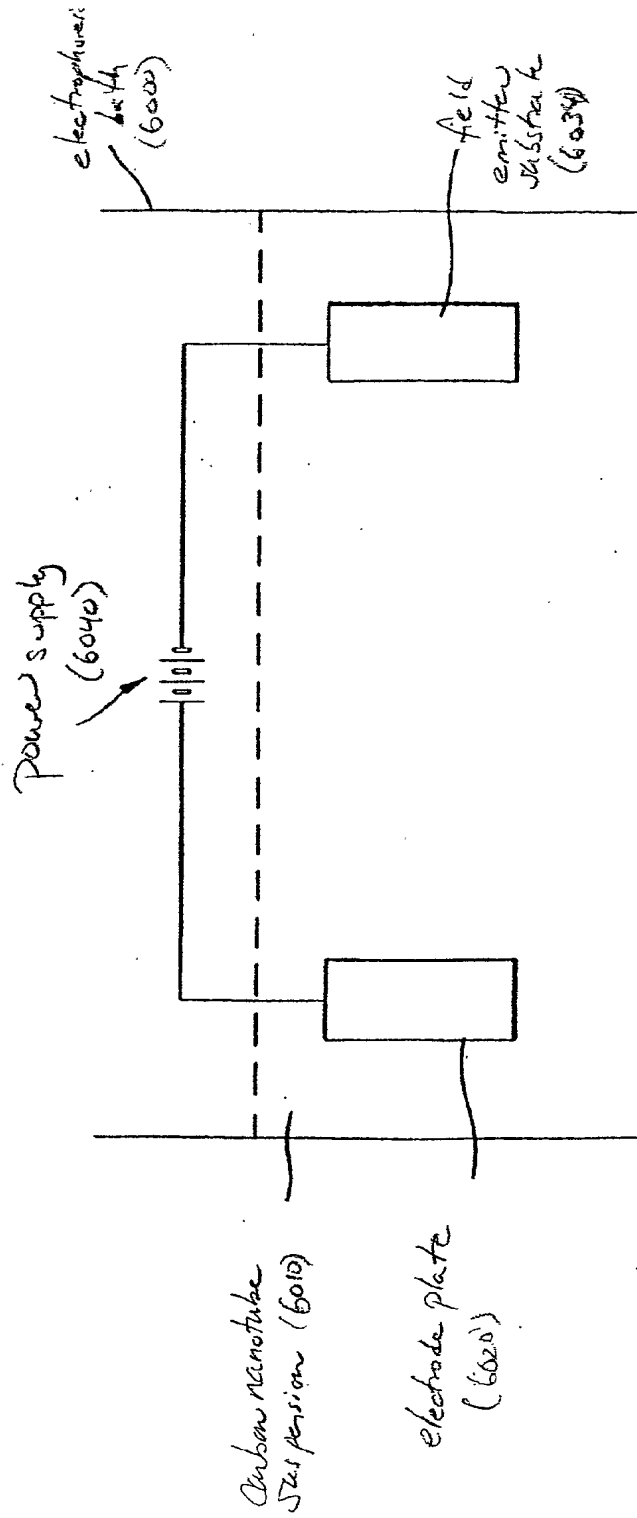


RCMSEC  
Osaka University

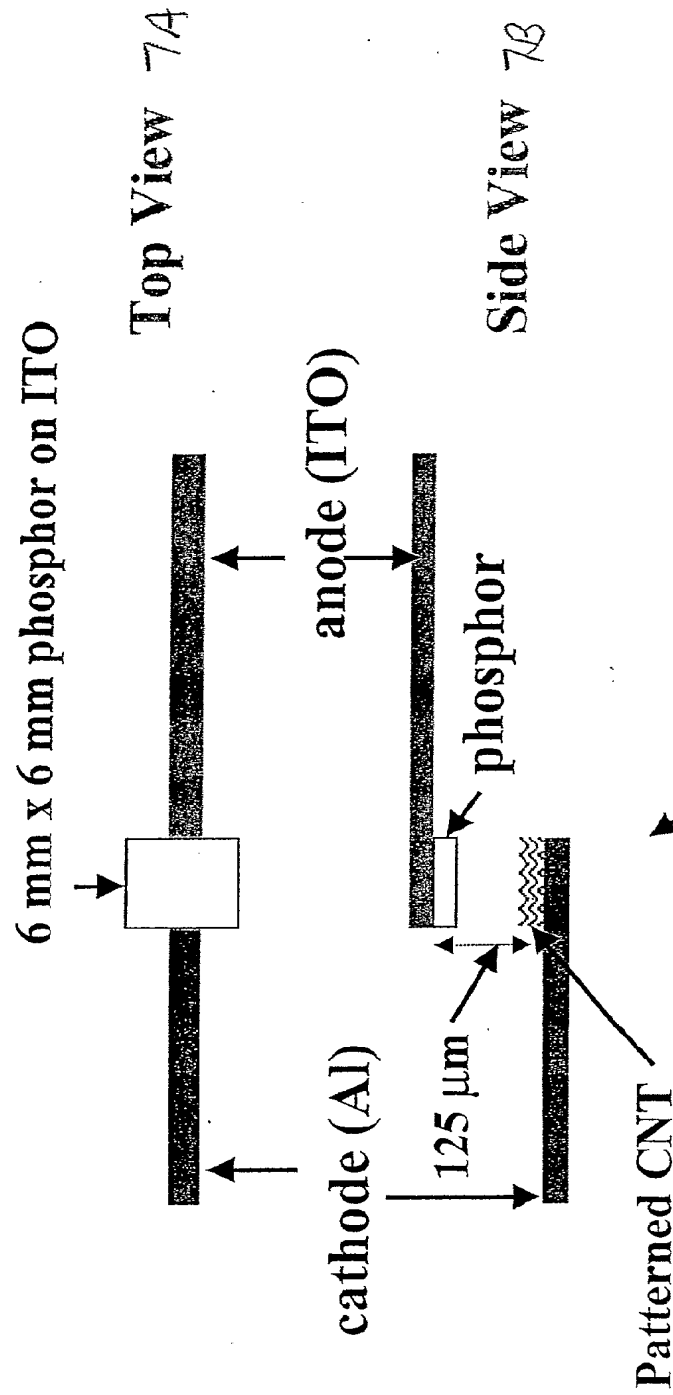
*M. Takai*

*CNT 2*

File 6



# Fig. 7 Schematic of Emission Measurement



Vacuum in emission chamber  $5 \times 10^{-9}$  Torr



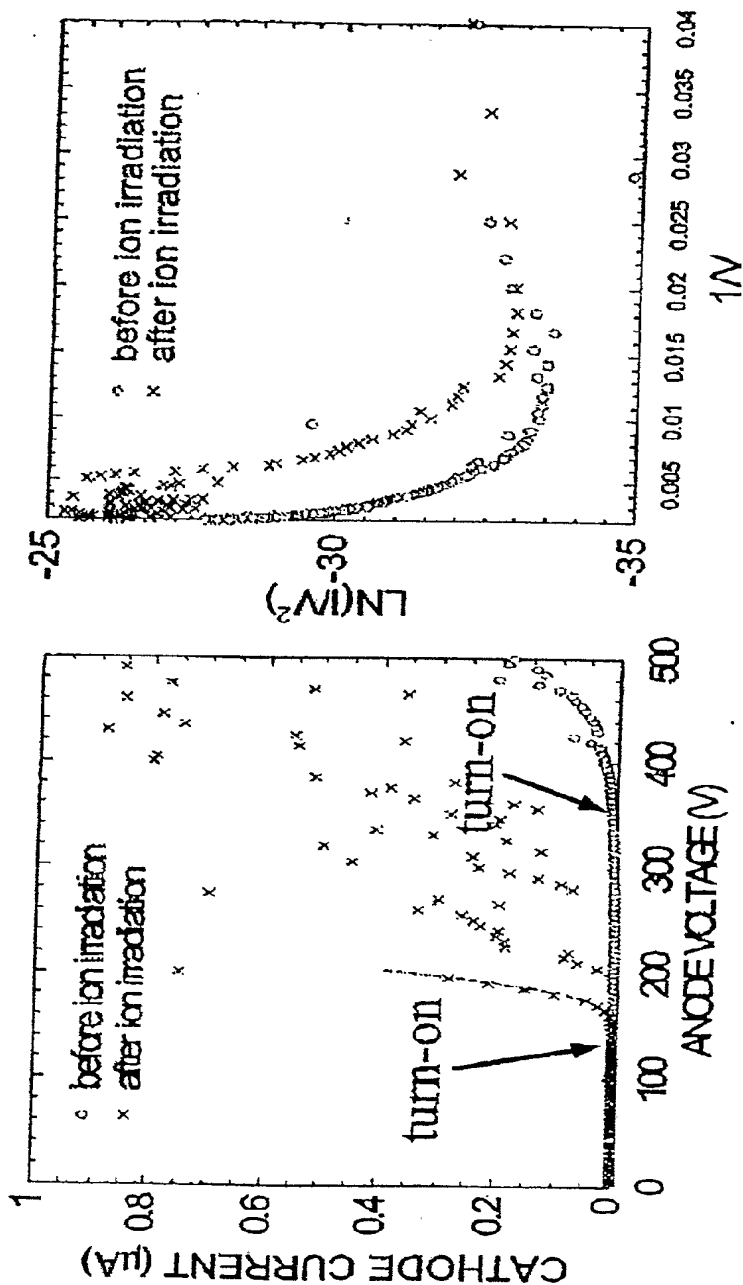
RCMSEC  
Osaka University

M. Takai

CNT 1

# Emission Characteristics Before and After Ion Irradiation

Fig 9



I-V characteristics

F-N plot

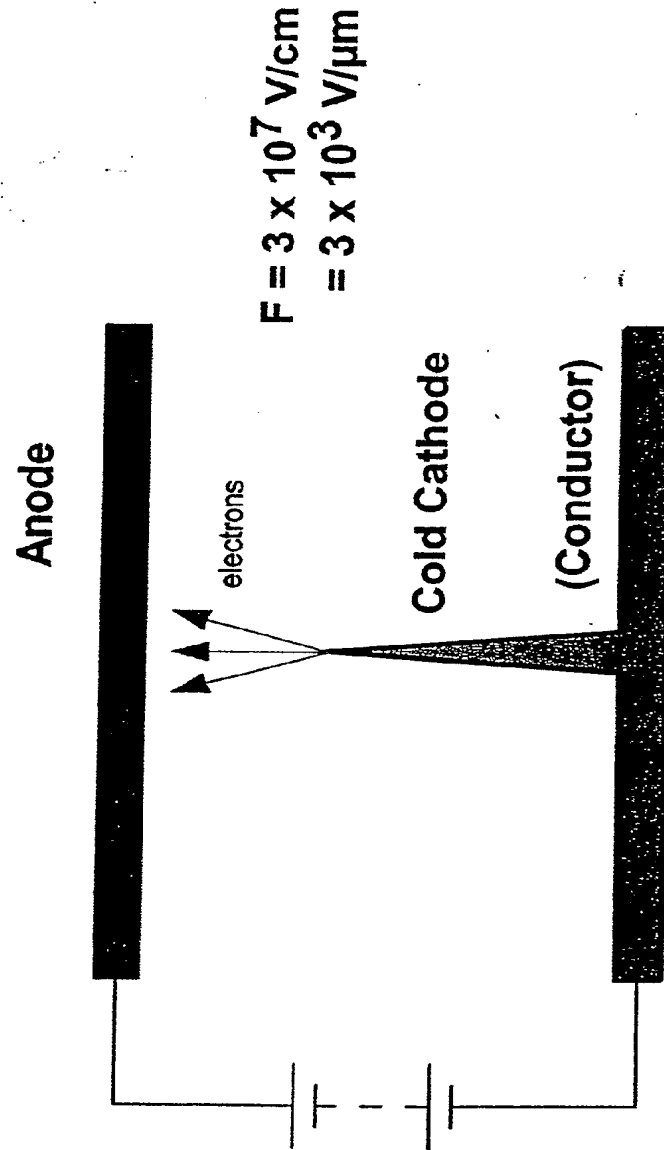


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CNT FEA 3

Fig. 10

# Classical Field Emitter



Observation by R.W. Wood (1897)  
Theory by Fowler and Nordheim (1928)

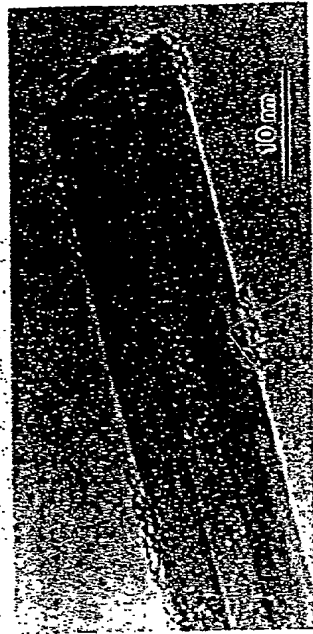
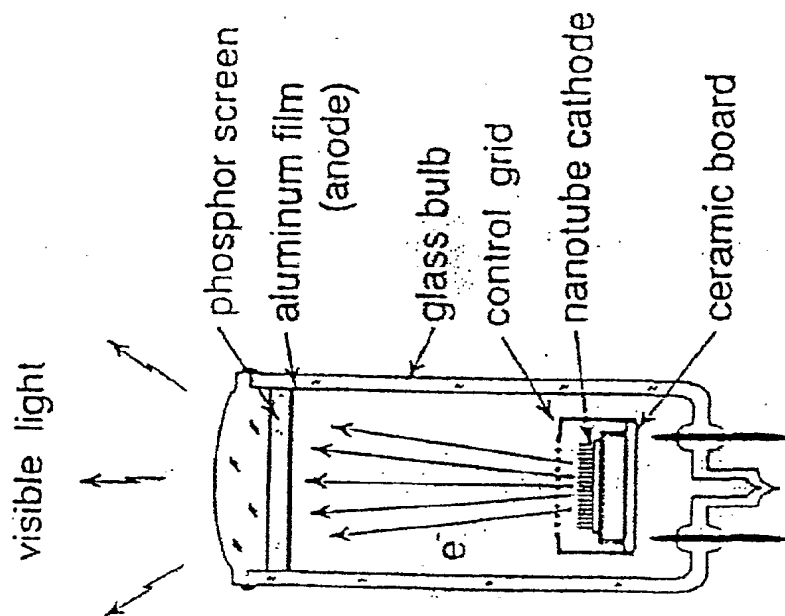


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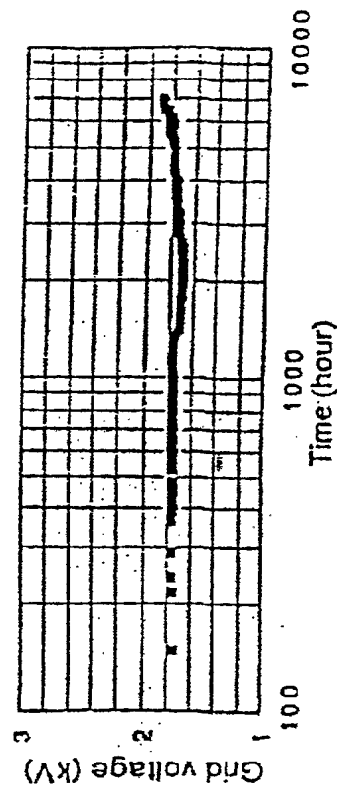
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Fig. 11

# FED with Carbon Nano Tubes



Multi-Wall CNT (MWCNT)



Life of FED with CNT

Shimojo (Ise Electronics Corp.)

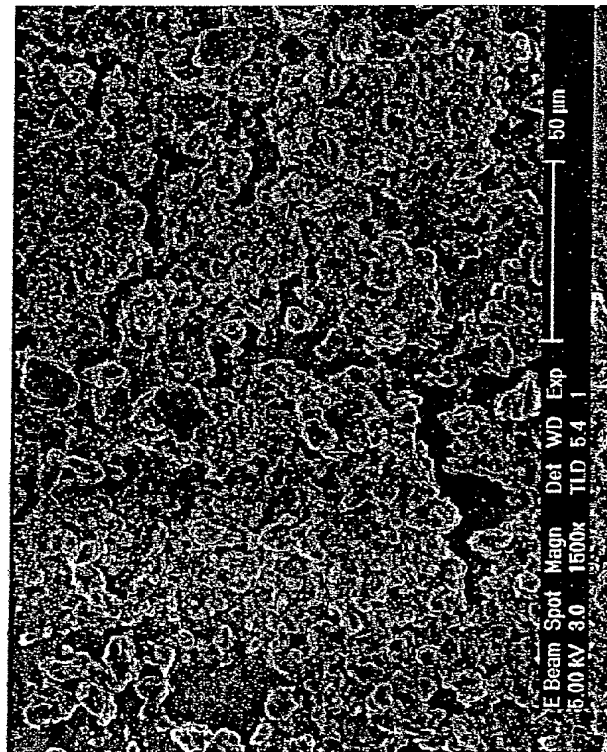


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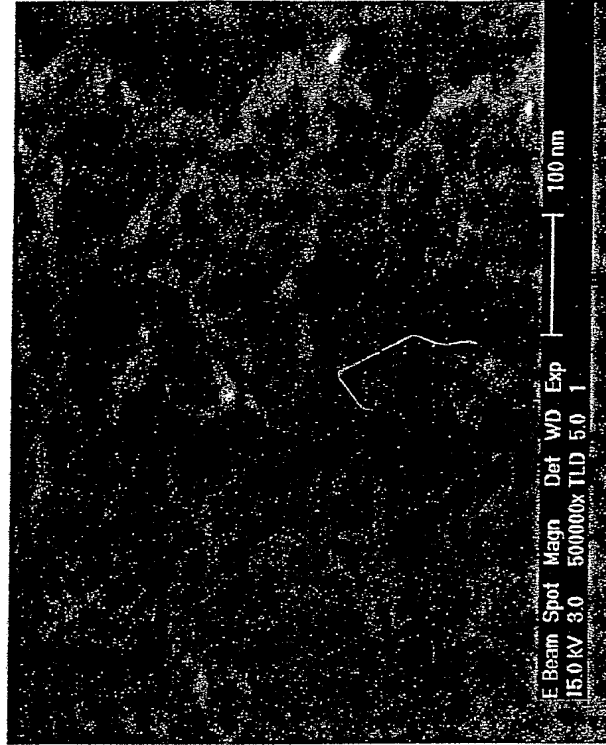
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Fig. 12

# SEM Views of CNT on Al



X 1,500



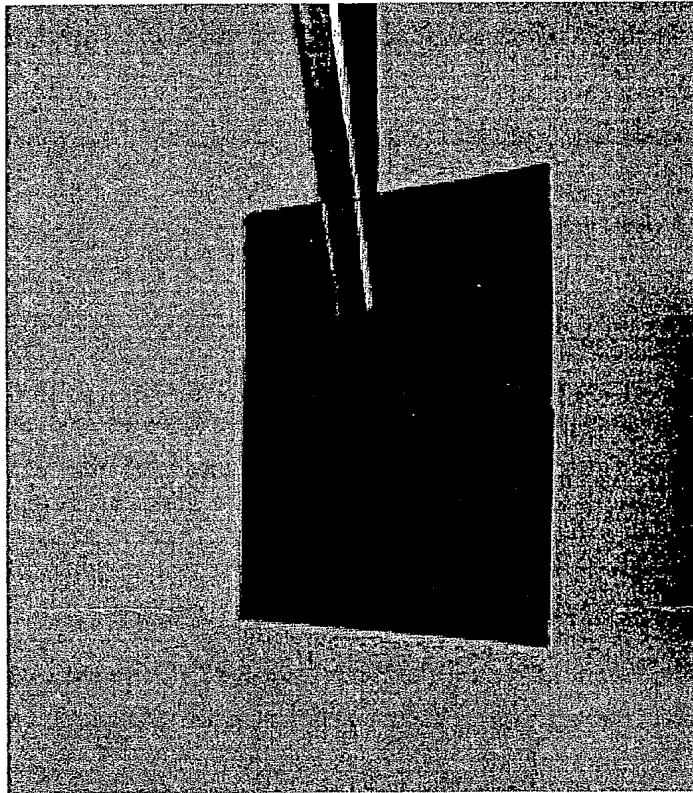
X 500,000



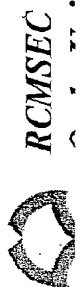
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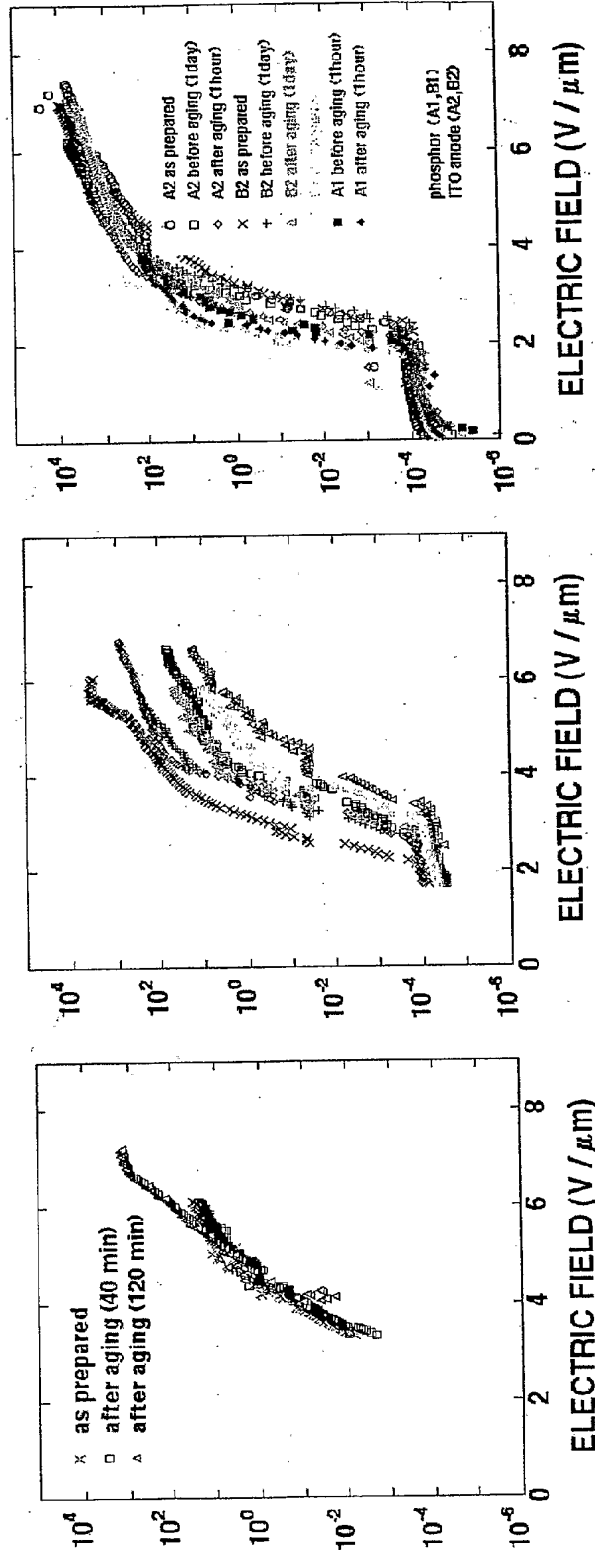
# CNT Mat



CNT-MAT



# Electron Emission Behavior



Electrophoresis

Screen Printing

CNT-MAT

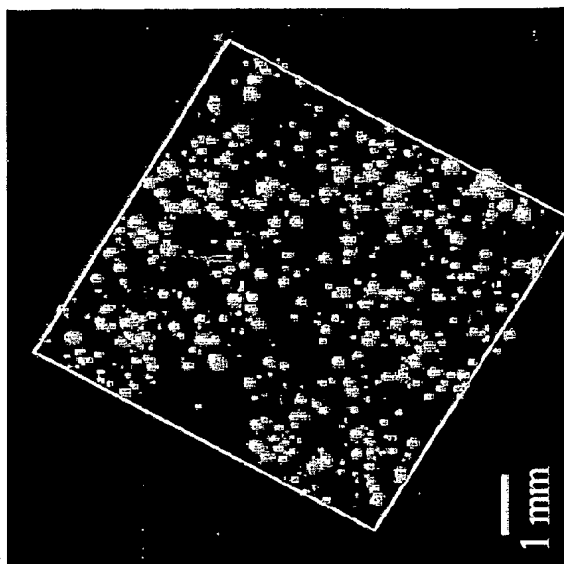
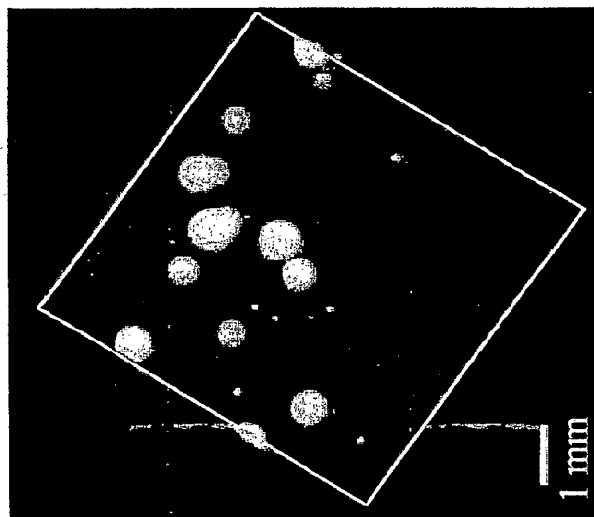
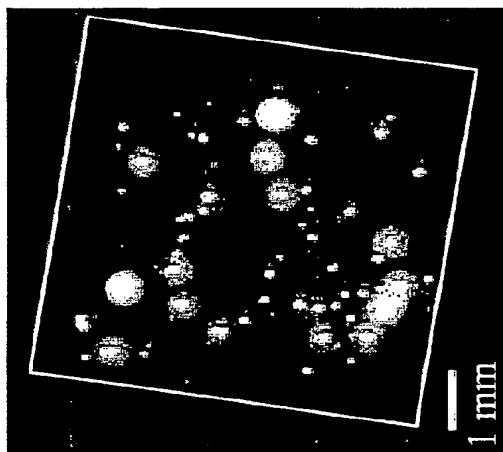


# Electron Emission Patterns

Electrophoresis

Screen Printed

CNT-MAT

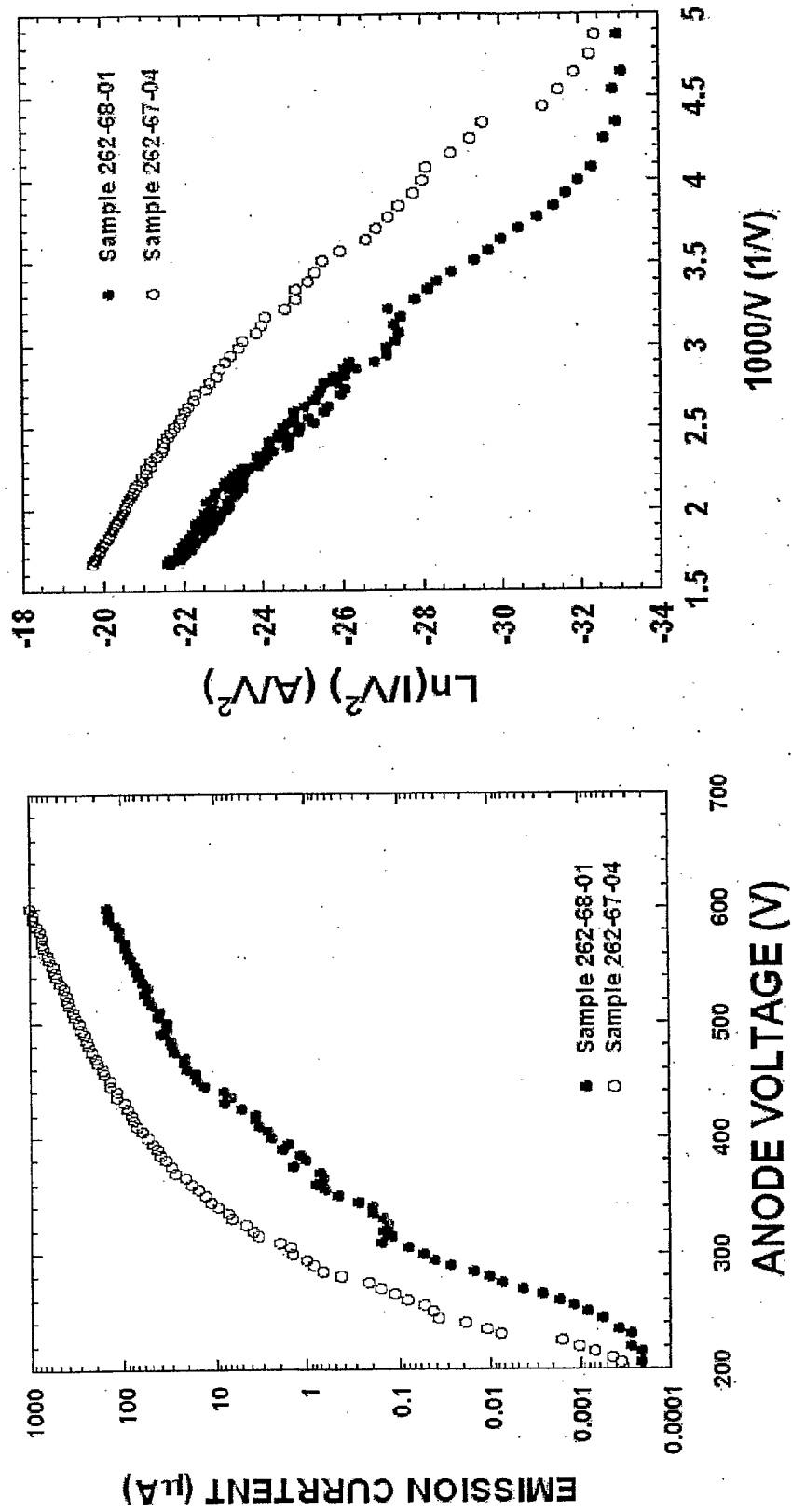


Applied Field 11.1 V/ $\mu$ m  
 Emission Current 230  $\mu$ A  
 Current Density 639  $\mu$ A/cm<sup>2</sup>

3.8 V/ $\mu$ m  
 145  $\mu$ A  
 402  $\mu$ A/cm<sup>2</sup>

7.1 V/ $\mu$ m  
 284.5  $\mu$ A  
 790  $\mu$ A/cm<sup>2</sup>

# Emission Characteristics of Inkjet Printed CNT

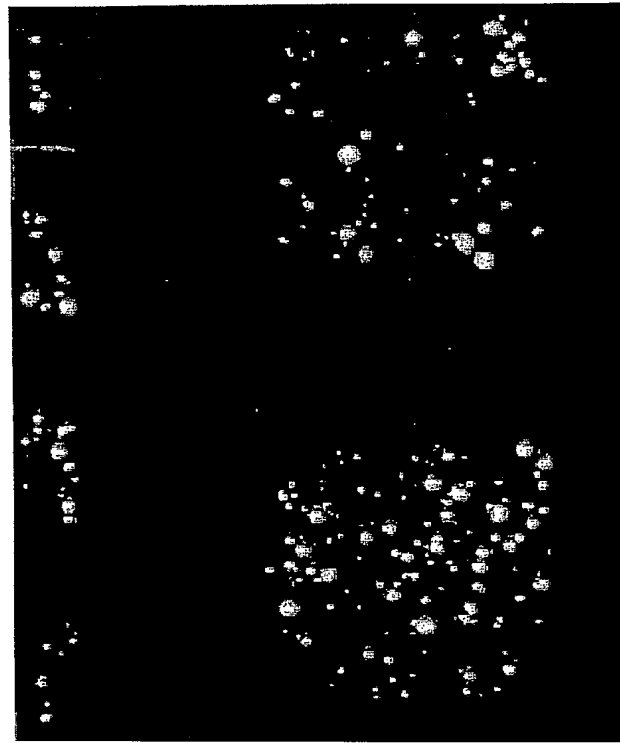


Gap between cathode and anode is 150  $\mu\text{m}$

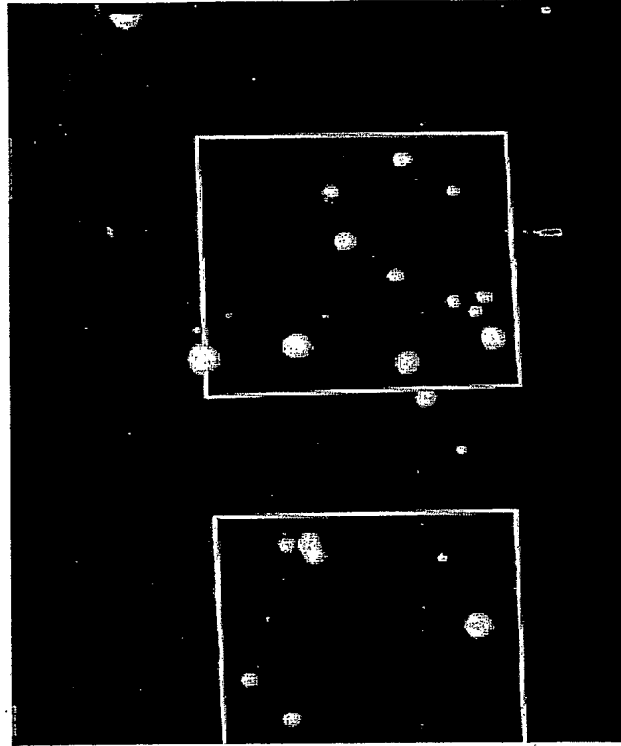


RCMSEC

# Emission Patterns from Inkjet Printed CNT

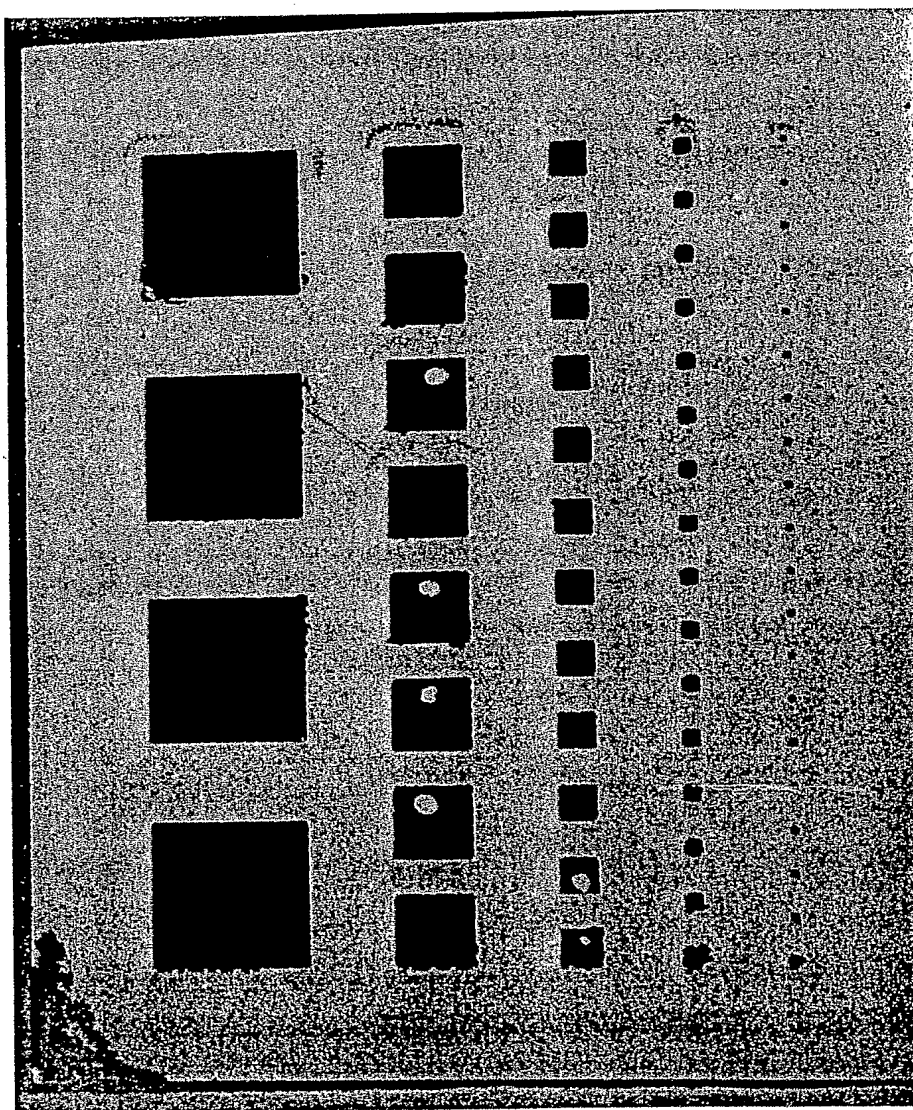


Sample 262-67-04



Sample 262-68-01

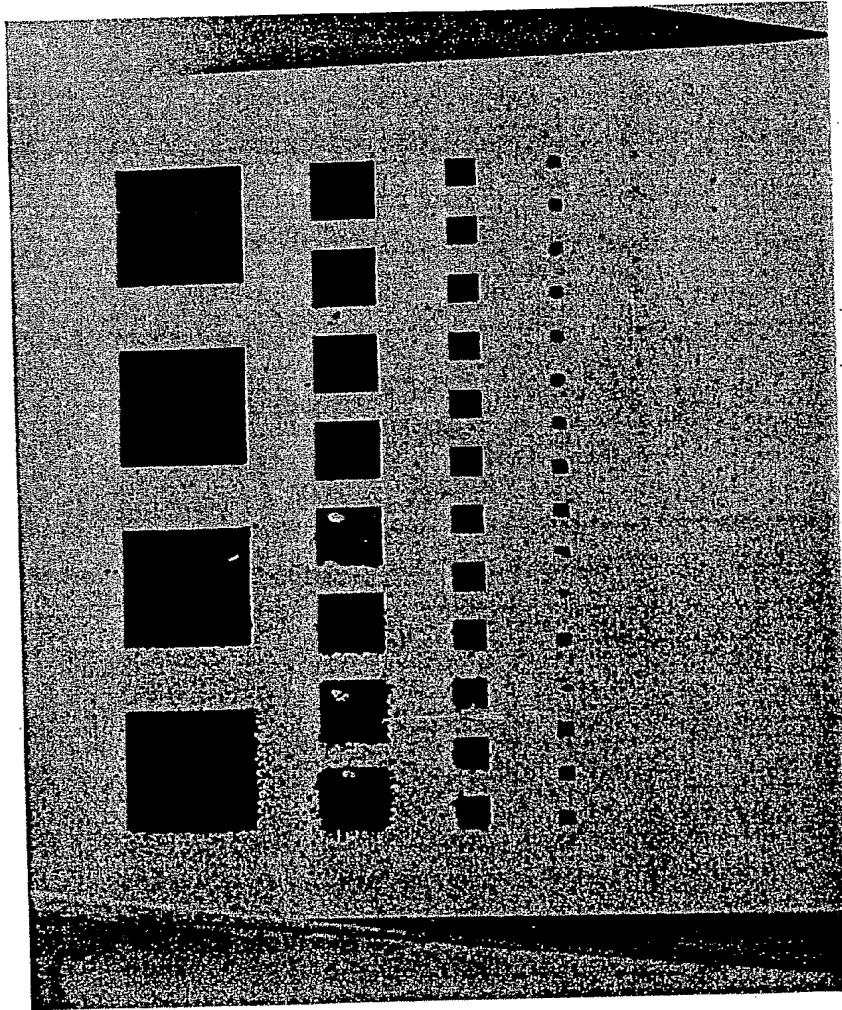
# Inkjet Printed CNT Cathode



Sample 262-67-01

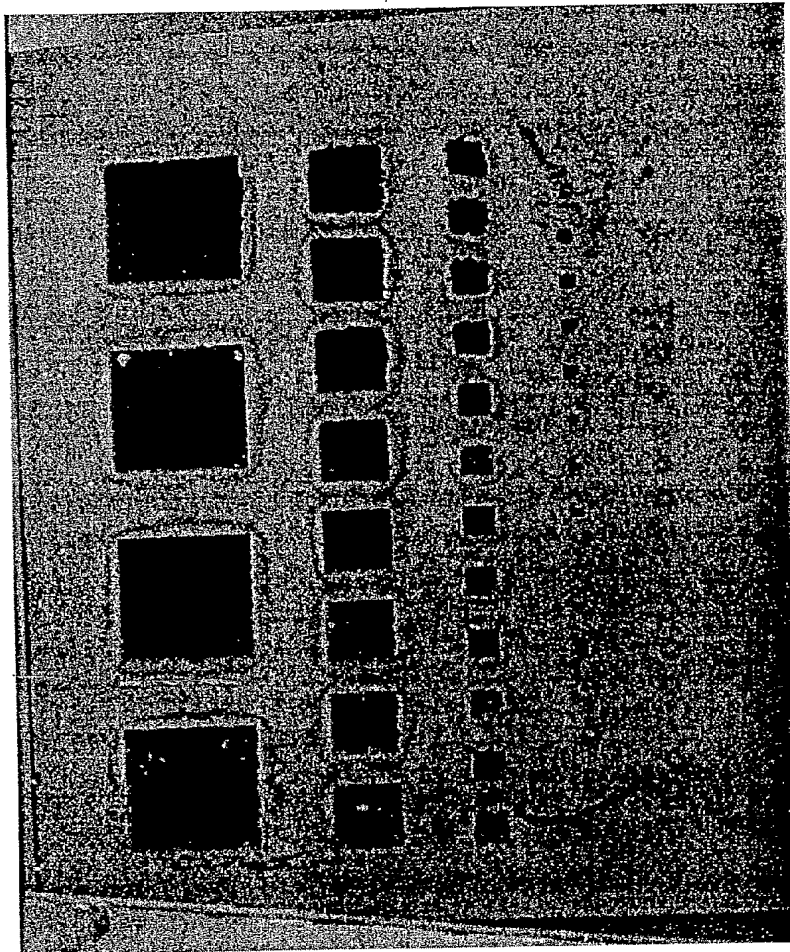


# Inkjet Printed CNT Cathode



Sample 262-67-02

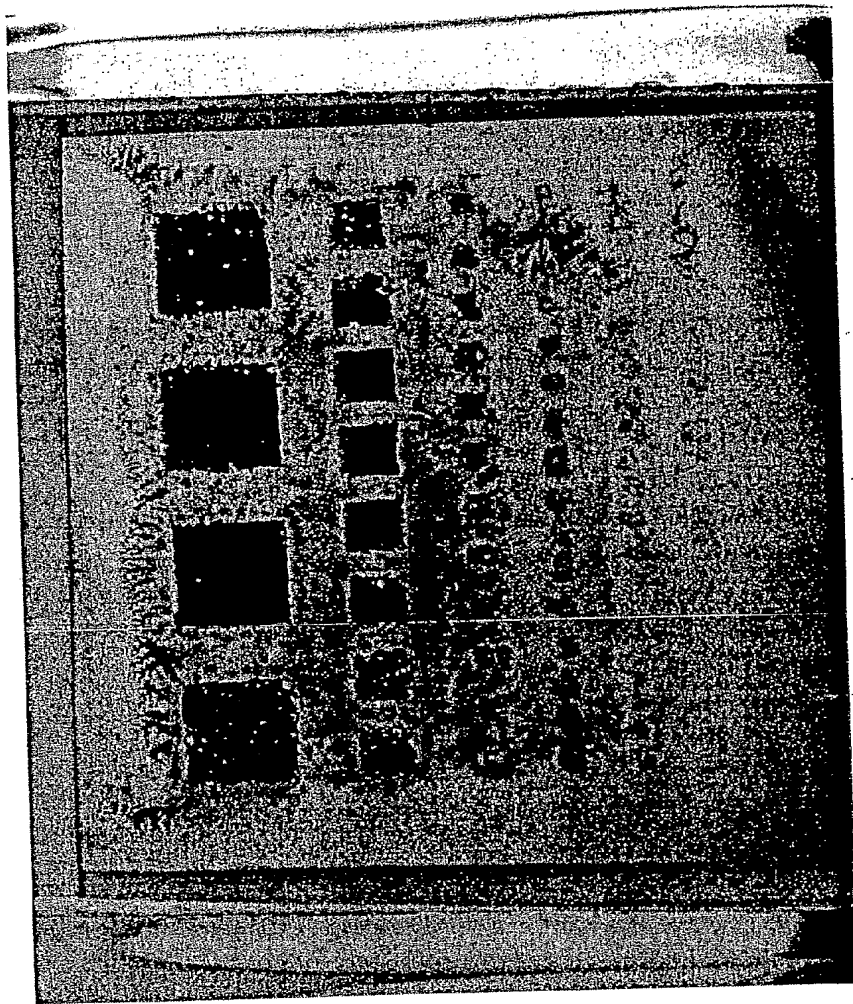
# Inkjet Printed CNT Cathode



Sample 262-67-04



# Inkjet Printed CNT Cathode



Sample 262-68-01

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
16 October 2003 (16.10.2003)

PCT

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**WO 2003/084865 A3**

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9/02, 1/304, 1/30, 19/24

(21) International Application Number:  
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(30) Priority Data:  
60/298,193 14 June 2001 (14.06.2001) US

(71) Applicant: **HYPERION CATALYSIS INTERNATIONAL, INC.** [US/US]; 38 Smith Place, Cambridge, MA 02138 (US).

(72) Inventors: **TAKAI, Mikio**; 4-15 Nakayamasoen, Takarazuka, Hyogo 665-0868, Osaka (JP). **FISCHER, Alan, B.**; 80 Antrim Street, Cambridge, MA 02139 (US). **NIU, Chunming**; 81 Fottler Avenue, Lexington, MA 02420 (US). **TENNENT, Howard, G.**; 301 Chandler Mill Road, Kennett Square, PA 19348 (US). **HOCH, Robert**; 1011 Route 296, Hensonville, NY 12439 (US). **BIEBUYCK, Hans**; 1 Sterling Court, Rockville, MD 20850 (US).

(74) Agents: **EVANS, Barry** et al.; Kramer Levin Naftalis & Frankel LLP, 919 Third Avenue, New York, NY 10022 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

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**Published:**

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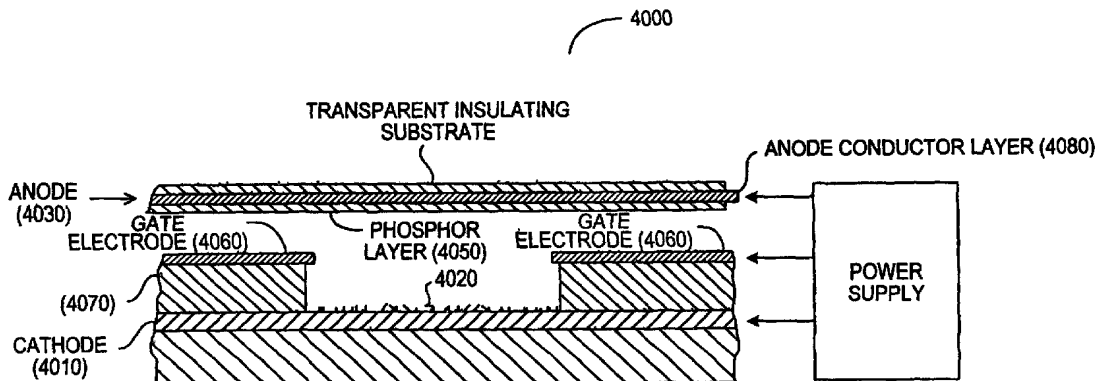
**(15) Information about Correction:**

**Previous Correction:**

see PCT Gazette No. 20/2004 of 13 May 2004, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FIELD EMISSION DEVICES USING MODIFIED CARBON NANOTUBES



(57) Abstract: The present invention relates to a field emission device (4000) comprising an anode (4080) and a cathode (4010), wherein the cathode includes carbon nanotubes (4020) which have been subjected to energy, plasma, chemical, or mechanical treatment. A method of treating the carbon nanotubes (4020) and for creating a field emission cathode (4010) is also disclosed. A field emission display device (4000) containing carbon nanotubes which have been subject to such treatment is further disclosed.

WO 2003/084865 A3

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/19021

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01J 9/00, 9/02, 1/304, 1/30, 19/24  
US CL : 313/309, 310, 311, 336, 351; 445/49, 50, 51; 427/78

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 313/309, 310, 311, 336, 351; 445/49, 50, 51; 427/78

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category *        | Citation of document, with indication, where appropriate, of the relevant passages        | Relevant to claim No.   |
|-------------------|---|---|
| X<br>---<br>Y     | JP 2001-110303 A (SAMSUNG SDI CO., LTD.) 20 April 2001 (20.04.2001), see entire document. | 1, 27, 50, 72, 78, 79<br>-----<br>2-26, 28-49, 51-71, 73-76   |
| X,P<br>---<br>Y,P | JP 2001-180920 A (SAMSUNG SDI CO LTD) 03 July 2001 (03.07.2001) see entire document.      | 1-7, 9, 13, 20, 21, 23,<br>25-28, 30-33, 35, 39,<br>46, 47, 49, 72, 78, 79<br>-----<br>8, 14-19, 22, 24, 29,<br>34, 36-38, 40-45, 48,<br>50-71, 73-76 |

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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| "P" document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search  
25 March 2004 (25.03.2004)

Date of mailing of the international search report  
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*Mariceli Santiago*

# INTERNATIONAL SEARCH REPORT

PCT/US02/19021

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category *    | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.   |
|---------------|--|---|
| X<br>---<br>Y | JP 2000-340098 A (NEC CORP) 08 December 2000 (08.12.2000) see entire document.     | 1, 2, 5, 7, 8, 13, 23,<br>24, 26-28, 31, 33, 34,<br>49, 72-76, 78, 79<br>-----<br>3, 4, 6, 9, 15-22, 25,<br>29, 30, 32, 35, 36,<br>39, 41-48, 50-58, 62,<br>64-71 |
| Y             | US 6,090,363 A (GREEN et al) 18 July 2000 (18.07.2000) see entire document.        | 1-6, 10-12, 15-22, 27-<br>32, 36-38, 41-55, 59-<br>61, 64-76, 78, 79  |
| Y             | JP 07-172807 A (NEC CORP) 11 July 1995 (11.07.1995) see entire document.           | 1-9, 13, 15-35, 39,<br>41-58, 62, 64-76, 78,<br>79  |
| X<br>---<br>Y | EP 1046613 A2 (JANG et al) 25 October 2000 (25.10.2000) see entire document.       | 1, 14, 27, 40, 49, 72,<br>78, 79<br>-----<br>2-6, 15-22, 28-32, 41-<br>48, 50-55, 63-71   |

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/19021

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claim Nos.: 77  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
Claims 77 depends from non-existing claim 107.
3. ☐ Claim Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐  
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

CORRECTED VERSION

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Organization  
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(54) Title: FIELD EMISSION DEVICES USING MODIFIED CARBON NANOTUBES

(57) Abstract: The present invention relates to a field emission device comprising an anode and a cathode, wherein said cathode includes carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment. The present invention also relates to a field emission cathode comprising carbon nanotubes which have been subject to such treatment. A method for treating the carbon nanotubes and for creating a field emission cathode is also disclosed. A field emission display device containing carbon nanotube which have been subject to such treatment is further disclosed.



WO 2003/084865 A2

## **Field Emission Devices Using Modified Carbon Nanotubes**

This application claims the benefit of U.S. Provisional Application No. 60/298,193, filed June 14, 2001, hereby incorporated by reference.

### **Field of Invention**

The present invention relates to field emission cathodes which use carbon nanotubes.

### **Background of the Invention**

Field emission devices are devices that capitalize on the movement of electrons. A typical field emission device includes at least a cathode, emitter tips, and an anode spaced from the cathode. A voltage is applied between the cathode and the anode causing electrons to be emitted from the emitter tips. The electrons travel in the direction from the cathode to the anode.

These devices can be used in a variety of applications including, but not limited to, microwave vacuum tube devices, power amplifiers, ion guns, high energy accelerators, free electron lasers, and electron microscopes, and in particular, flat panel displays. Flat panel displays can be used as replacements for conventional cathode ray tubes. Thus, they have application in television and computer monitors.

Conventional emitter tips are made of metal, such as molybdenum, or a semiconductor such as silicon. The problem with metal emitter tips is that the control voltage required for emission is relatively high, e.g., around 100 V. Moreover, these emitter tips lack uniformity resulting in non-uniform current density between pixels.

More recently, carbon materials, have been used as emitter tips. Diamond has negative or low electron affinity on its hydrogen-terminated surfaces. Diamond tips, however, have a tendency for graphitization at increased emission currents, especially at currents about thirty mA/cm<sup>2</sup>. Carbon nanotubes, also known as carbon fibrils, have been the latest advancement in

emitter tip technology. Although much work has been done in the area of carbon nanotubes as emitter tips in field emitting technologies, substantial improvement is still needed, specifically, in three areas. These areas are reducing work voltage, increasing emission current, and increasing emission sites.

Reducing the work voltage increases the ease of electron emission and also increases the longevity of the emitter tips. Increasing both the emission current and the number of emission sites increase the brightness.

### **Objects of the Invention**

It is an object of the present invention to provide improved field emission cathodes comprising carbon nanotubes as the emitters, which operate at reduced working voltage, have increased emissions and more emission sites.

It is a further object of this invention to provide improved field emission cathodes where the emitters comprise treated carbon nanotubes.

It is yet a further object of this invention to provide methods for manufacturing improved field emission cathodes by screen or ink-jet printing of substrates with inks containing treated or untreated carbon nanotubes.

It is still a further object of this invention to provide improved field emission display devices having improved properties such as reduced working voltage, increased emissions and more emission sites.

### **Summary of the Invention**

The present invention relates to a field emission cathode comprising carbon nanotubes, wherein the nanotubes have been subjected to an energy, chemical, plasma or mechanical



treatment. The carbon nanotubes may form the cathode or may be deposited onto a substrate to form the cathode.

This invention also relates to a field emission device comprising an anode and a cathode which has been subject to such a treatment.

In one embodiment, the field emission device comprises a substrate, a porous top layer positioned on said substrate, a catalyst material positioned on said layer and a cathode positioned on said catalyst material, said cathode including a bundle of carbon nanotubes which have been subjected to a treatment as described above.

The present invention also includes various field emission display devices. In one embodiment, the field emission display device comprises a first substrate, a first metal film on said first substrate; a conductive polymer film on said first metal film, said conductive polymer film including emitter tips comprising carbon nanotubes which have been subject to a treatment as described above; a dielectric film on said first metal film; a second metal film on said dielectric film; a spacer; a transparent electrode separated from said second metal film by said spacer; a fluorescent material on one side of said transparent electrode; a second substrate on the other side of said transparent electrode; and a power supply.

In an alternative embodiment, the field emission display device comprises a cathode including carbon nanotubes which have been subjected to a treatment as described above; an insulating layer on said cathode; a gate electrode on said insulating layer; an anode spaced from said cathode comprising a phosphor layer, an anode conducting layer and a transparent insulating substrate; and a power supply.

The carbon nanotubes used in the cathodes and field emission devices of the invention may be single wall or multi-wall. They comprise substantially cylindrical carbon fibrils having

one or more graphitic layers concentric with their cylindrical axes, are substantially free of pyrolytically deposited carbon overcoat, have a substantially uniform diameter between 1 nm and 100 nm and have a length to diameter ratio greater than 5. The carbon nanotubes may be in form of aggregates such as cotton candy aggregates or bird nest aggregates, as well as in the form of a mat or a film.

Energy treatments may include ion beams, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam. Plasma treatment may be performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof. Chemical treatment may include acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

The field emission cathode may be formed by dispersing carbon nanotubes into a liquid vehicle to form a solution; transferring said solution to an electrophoresis bath, said bath including an anode and a cathode immersed therein; applying a voltage to said anode and said cathode, thereby causing said carbon nanotubes to deposit onto said cathode; removing said cathode from said bath; heating said cathode; and subjecting such cathode to a treatment as described above.

### **Brief Description of the Drawings**

The accompanying drawings, illustrate an exemplary embodiment of the present invention.

Figure 1 is a cross-sectional view of a field emission display device using an modified carbon nanotube cathode according to an exemplary embodiment of the present invention;

Figure 2 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 3 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 4 is a cross-sectional view of a field emission display device using modified carbon nanotubes according to another exemplary embodiment of the present invention;

Figure 5 illustrates an electrophoresis bath used to fabricate a carbon nanotube film (electrode);

Figure 6 illustrates another electrophoresis bath used to fabricate a carbon nanotube film (electrode);

Figure 7 illustrates a schematic to measure the differences between treated (modified) and untreated field emission characteristics;

Figure 8 is a plot showing cathode current as a function of voltage for modified carbon nanotubes versus untreated nanotubes in a field emission device;

Figure 9 is a Fowler-Nordheim plot for modified carbon nanotubes and untreated nanotubes in a field emission device.

Figure 10 illustrates a classical field emitter;

Figure 11 illustrates a field emitting device using ion bombarded carbon nanotubes;

Figure 12 is a SEM view of the carbon nanotubes on the aluminum substrate.

Figure 13 illustrates a carbon nanotube mat;

Figure 14 illustrates the electron emission behavior of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats in the form of plots of current density as a function of the electric field.

Figure 15 is a series of photographs of electron emission patterns of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats.

Figure 16 is a series of plots of emission characteristics of inkjet printed carbon nanotubes.

Figure 17 is a series of photographs of electron emission patterns from sample inkjet printed carbon nanotubes.

Figure 18 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-01.

Figure 19 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-02.

Figure 20 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-67-04.

Figure 21 is a photograph of several inkjet printed carbon nanotube cathodes made from sample 262-68-01.

### **Detailed Description of the Invention**

All referenced patents, patent applications, and publications are incorporated by reference herein.

### **Definitions**

“Aggregate” refers to a microscopic particulate structures of nanotubes.

“Assemblage” refers to nanotube structures having relatively or substantially uniform physical properties along at least one dimensional axis and desirably having relatively or substantially uniform physical properties in one or more planes within the assemblage, i.e. having isotropic physical properties in that plane. The assemblage can comprise uniformly

dispersed individual interconnected nanotubes or a mass of connected aggregates of nanotubes. In other embodiments, the entire assemblage is relatively or substantially isotropic with respect to one or more of its physical properties.

“Carbon fibril-based ink” refers to an electroconductive composite in which the electroconductive filler is carbon fibrils.

“Graphenic” carbon is a form of carbon whose carbon atoms are each linked to three other carbon atoms in an essentially planar layer forming hexagonal fused rings. The layers are platelets having only a few rings in their diameter or ribbons having many rings in their length but only a few rings in their width.

“Graphenic analogue” refers to a structure which is incorporated in a graphenic surface.

“Graphitic” carbon consists of layers which are essentially parallel to one another and no more than 3.6 angstroms apart.

“Nanotube”, “nanofiber” and “fibril” are used interchangeably. Each refers to an elongated hollow carbon structure having a diameter less than 1  $\mu\text{m}$ . The term “nanotube” also includes “bucky tubes” and graphitic nanofibers in which the graphene planes are oriented in herring bone pattern.

The terms “emitter tips” and “emitters” are interchangeable. The use of the word “tip” is not meant to limit the emission of the electrons only to the tips of the carbon nanotubes. The electrons can be emitted from any part of the carbon nanotubes.

### **Carbon Nanotubes**

Carbon nanotubes (CNTs) are vermicular carbon deposits having diameters of less than five hundred nanometers. They exist in a variety of forms, and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces, by high

temperature carbon arc processes, where solid carbon is used as the carbon feed stock, and by simultaneous laser vaporization of graphite rods and a transition metal. Tennent, U.S. Patent No. 4,663,230, succeeded in growing small diameter nanotubes having cylindrical ordered graphite cores and an ordered "as grown" graphitic surface uncontaminated with pyrolytic carbon.

Tennent, describes carbon nanotubes that are free of a continuous thermal carbon overcoat and have multiple graphitic outer layers that are substantially parallel to the fibril axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the curved layers of graphite, substantially perpendicular to their cylindrical axes. They generally have diameters no greater than 0.1 micron and length to diameter ratios of at least five. Such nanotubes having graphitic layers that are substantially parallel to the fibril axis and diameters between 3.5 and 75 nanometers, are described in Tennent et al., U.S. Pat. No. 5,165,909 and Tennent et al, U.S. Pat. No. 5,171,560.

The graphitic planes may also be oriented at an angle to the fibril axis. Such structures are often called "fishbone" fibrils or nanotubes because of the appearance of the two dimensional projection of the planes. Such morphologies and methods for their production are discussed in U.S. Patent No. 4,855,091 to Geus, hereby incorporated by reference.

Assemblages and composites consisting of multiwall nanotubes have been described in Tennent et al, U.S. Patent No. 5,691,054. Such assemblages and composites are composed of randomly oriented carbon fibrils having relatively uniform physical properties. Furthermore, these multiwall nanotubes are substantially free of pyrolytically deposited carbon.

The carbon nanotubes disclosed in U.S. Patents Nos. 4,663,230, 5,165,909, and 5,171,560, may have diameters that range from about 3.5 nm to 70 nm and lengths greater than 100 times the diameters, an outer region of multiple essentially continuous layers of ordered

carbon atoms and a distinct inner core region. Simply for illustrative purposes, a typical diameter for a carbon fibril may be approximately between about 7 and 25 nm, and a typical range of lengths may be 1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

As disclosed in U.S. Pat. No. 5,110,693 and references therein, two or more individual carbon fibrils may form microscopic aggregates of entangled fibrils. These aggregates can have dimensions ranging from 5 nm to several cm. Simply for illustrative purposes, one type of microscopic aggregate ("cotton candy or CC") resembles a spindle or rod of entangled fibers with a diameter that may range from 5 nm to 20  $\mu\text{m}$  with a length that may range from 0.1  $\mu\text{m}$  to 1000  $\mu\text{m}$ . Again for illustrative purposes, another type of microscopic aggregate of fibrils ("birds nest, or BN") can be roughly spherical with a diameter that may range from 0.1  $\mu\text{m}$  to 1000  $\mu\text{m}$ . Larger aggregates of each type (CC and/or BN) or mixtures of each can be formed.

Recently carbon nanotubes having a single wall comprising graphite have been produced. These single wall carbon nanotubes have been described in Bethune et al., U.S. Pat. No. 5,424,054; Guo, et al., Chem. Physics Lett., 243:1-12 (1995); Thess, et al, Science, 273:483-487 (1996); Journet et al., Nature 388 (1997) 756; Vigolo, et al., Science 290 (2000) 1331. They are also described in U.S. Patent Application Serial No. 08/687,665, entitled "Ropes of Single-Walled Carbon Nanotubes" herein incorporated by reference.

Additional methods of producing single wall nanotubes production have been described in PCT Application No. PCT/US99/25702 and PCT Application No. PCT US98/16071 herein incorporated by reference.

Single wall nanotubes are useful in a variety of applications. The tubular structure imparts superior strength, low weight, stability, flexibility, thermal conductivity, large surface area and a host of electronic properties. They can be used as reinforcements in fiber reinforced

composite structures or hybrid composite structures, i.e., composites containing reinforcements such as continuous fibers in addition to single wall nanotubes.

The carbon nanotubes may be treated in their as-made form or may be deposited as a film on a suitable substrate and then treated.

#### **Preparation of Films Containing Carbon Nanotubes**

The carbon nanotubes used were obtained from Hyperion Catalysis International, Cambridge Mass. They had the designations #1100 and #1100 L. Sample #1100 L comprised carbon nanotubes having a so-called BN macromorphology that had been ball milled in a Red Devil Shaking Ball Mill for approximately four hours. Some samples were treated with an acid wash of twelve grams of  $\text{H}_3\text{PO}_4$  in 1.5 liters of water at atmospheric reflux before ball milling. The carbon nanotubes were dried in an oven before ball milling.

#### **The Solution of Nanotubes**

The nanotubes were dispersed by known methods in a suitable solvent as is well known in the art, e.g. isopropyl alcohol.

#### **The Substrate**

Aluminum substrates were prepared by vapor depositing aluminum onto glass flats that were approximately 55 mm x 45 mm x 1 mm in its dimensions. Aluminum adhesion may be enhanced with the addition of an underlying vapor deposited adhesion layer. A dielectric mask can be applied to pattern the aluminum surface into a plurality of electrodes prior to nanotube deposition.

The aluminum can also be pretreated to promote the adhesion of the carbon nanotubes. This can be done with any known pretreatments of aluminum. The carbon nanotubes can also adhere to other substrates, e.g.,  $\text{SnO}_2$ -in/Sb



### **The Electrophoresis Bath**

The electrophoretic deposition of the carbon nanotubes was conducted in an electrophoresis bath. The bath consists of a chamber to contain the solution of carbon nanotubes and means for immersing two opposing electrodes separated by some distance with the carbon nanotubes between the opposing electrodes. A DC power supply, external to the bath, is used to apply a voltage between the two electrodes immersed in the bath. The cathode lead is connected to the patterned aluminum substrate and the anode lead is connected to the other electrode. Tantalum was used for the second metal. The voltage applied to the two electrodes can be adjusted to a suitable level or the voltage can be adjusted to obtain a suitable current between the two electrodes.

The attachment of carbon nanotubes to the aluminum can be enhanced by a binder. The binders can be a mixture of Ag paste, carbon nanotubes and ethanol. Or the binders can be a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

### **Electrophoretic Deposition of Carbon Nanotubes on the Substrate**

A field emitter substrate is loaded into the electrophoresis bath. A plurality of cathodes are arranged on a glass substrate, and a dielectric film is formed with holes over the cathodes. Metal gates with openings which are located over the holes of the dielectric film are formed to expose the surface of the cathodes. Then, the carbon nanotubes are uniformly deposited onto the obtained substrate, on the surface of the cathodes exposed through the holes by electrophoretic deposition at room temperature.

### **Post Deposition Heat Treatment**

After the deposition of carbon nanotube particles by electrophoresis, low-temperature heating is performed to sustain the deposition of the carbon nanotubes on the cathodes and

ensure easy removal of impurities which are incorporated into the field emitter during the deposition.

### **EXAMPLE I**

#### **Preparation of Nanotube Film on Aluminum Substrate**

With reference to Figure 5, a solution is formed that contains 150 ml i-propyl alcohol (IPA) and 0.44 grams of acid washed carbon nanotubes. This solution is placed in an electrophoresis bath 5000.

A patterned, aluminum coated glass substrate 5002 serves as one electrode in electrophoresis bath 5000. The pattern forms the pixel size. The smallest feature size can be ca. 1 micron. The aluminum coated glass 5002 is about 55 mm x 45 mm x 1 mm in its dimensions. The aluminum pattern size is about 9 mm x 9 mm. The other electrode, tantalum (Ta) electrode 5004 is also inserted into the electrophoresis bath 5000. A spacer 5006 separates the aluminum coated glass 5002 from the tantalum electrode 5004. A DC voltage, for example between 40 to 120 volts, e.g., 100 volts is applied to the electrodes. A current between 1.0 to 5 mA, e.g., 3.8 mA, is observed between the electrodes. The duration of the preparation time can be between about 30 to about 90 minutes, e.g., 60 minutes.

Figure 6 illustrates an alternative electrophoretic method of creating the film according to the method disclosed in UK patent application 2,353,138 described below. First, a carbon nanotube suspension is created. The carbon nanotube particles can have lengths from about 0.1 to about 1  $\mu\text{m}$ . The suspension can also include a surfactant, e.g. an anionic, ionic, amphoteric or nonionic, or other surfactant known in the art. Examples of suitable surfactants include octoxynol, bis(1-ethylhexyl)sodium sulfosuccinate, and nitrates of  $\text{Mg}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$  and  $\text{La}(\text{OH})_3$ .

The suspension is then sonicated to charge the carbon nanotube particles. The intensity of the electric field and the time for which the electric field is applied define the thickness of the carbon nanotube layer. Greater intensity and longer time yield thicker layers.

With reference to Figure 6 the field emitter substrate 6030 is loaded into the electrophoresis bath 6000 containing a carbon nanotube suspension 6010. An electrode plate 6020 is also installed in the electrophoresis bath 6000 spaced apart from the field emitter substrate 6030. The cathode of a DC power supply 6040, which is installed outside of the electrophoresis bath 6000, is connected to the other cathodes of the field emitter substrate 6030 and the anode of the DC power supply 6040 is connected to the electrode plate 6020. Then, a bias voltage of about 1 to about 1000 volts is applied from the DC power supply 6040 between the electrode plate 6020 and the cathodes of the field emitter substrate 6030.

As a positive voltage of the DC power supply 6040 is applied to the electrode plate 6020, carbon nanotube particles charged by positive ions in the carbon nanotube suspension 6010 migrate to and are attached to the exposed cathodes of the field emitter substrate 6030, which results in the formation of a carbon nanotube film in the pattern of the exposed cathodes.

The height of the printed carbon nanotube film, also known as the ink, coating, or paste, may be less than 10 microns and the space which isolates carbon nanotube cathodes from the indium tin oxide anode with indium tin oxide and phosphor is about 125 microns.

The electrophoresis process can be applied to both diodes and triodes. For applications to a diode, an electric field having opposite charges to those on the surfaces of the carbon nanotube particles is applied to exposed electrode surface of a field emitter substrate for selective deposition of carbon nanotube particles thereon. For application to a triode having gates, a weak positive electric field is applied to the gates while a positive electric field is applied to the

electrodes of the field emitter substrate, which avoids deposition of carbon nanotube particles on the gates. In particular, the electrode plate is connected to the anode of the DC power supply and the cathodes of the field emitter substrate are connected to the cathode of the DC power supply. As a positive potential is applied to the gates, the gates repel positive ions in the carbon nanotube suspension at the surface, while the exposed cathodes of the field emitter substrate, which are connected to the cathode of the DC power supply, pull positive ions of the suspension through the holes. As a result, the carbon nanotubes are deposited only on the entire exposed surface of the cathodes, not on the gates of the field emitter substrate. At this time, carbon nanotube particles are attracted to the field emitter substrate and are oriented substantially horizontal, or substantially parallel to the substrate, which allows the carbon nanotube particles to smoothly migrate through the holes to the cathodes, and thus the carbon nanotubes can be deposited.

The film can also be prepared similarly to the carbon ink disclosed in European Patent Application EP 1 020 888 A1 - *Carbon ink, electron-emitting element, method for manufacturing and electron-emitting element and image display device*

#### **Alternative Methods to Prepare Carbon Nanotube Films**

In addition to electrophoresis, other processes such as screen printing can be used for creating the patterns. A screen printing process is disclosed in U.S. Patent No. 6,270,369. In addition to screen printing, the carbon nanotubes can be applied to a substrate by ink jet printing. Ink printing is accomplished with carbon nanotube based liquid media or inks in which the fibrils are nearly individualized. Inks typically contain a carrier liquid and carbon nanotubes, and may be dried (i.e. evaporate the carrier liquid).

The carbon nanotubes can also be deposited in the form of a mat. Such porous mats, having densities between 0.10 and 0.40 gm/cc are conveniently formed by filtration of

suspensions of nanotubes as described in US Patents Nos. 6,099,965 and 6,031,711. Oxidized nanotubes are easily dispersed in and then filtered from aqueous media. The mats may be subjected to a rigidization or cross linking step as discussed in the aforecited patents.

Carbon nanotube mat cathodes have uniform emission sites at relatively low applied field and may obtain a current density of more than 10 mA/cm<sup>2</sup>.

A comparison of the electron emission behavior of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats in the form of plots of current density as a function of the electric field is displayed in Figure 14. A further comparison of the electron emission patterns of electrophoretically deposited carbon nanotubes, screen printed carbon nanotubes and carbon nanotube mats is displayed in Figure 15.

#### **Carbon Nanotube Based Inks**

In yet another method, fibril based inks can be formulated for use in spray equipment. When combined with a masking technology, spray painting of fibril based inks offers a suitable method for depositing fibril ink patterns of either simple or complex designs. Spray painting can also be used to apply a uniform coating over a large area, with or without a masking technology. Spraying equipment can accommodate inks/paints with a wide range of viscosity and thixotropy. Airbrushes are a type of sprayer widely used in the graphic arts industry and areas where fine detailed spraying is desired.

The inks are sprayed through a stencil (i.e., mask, layer with cut out pattern, etc.) to form the corresponding pattern on the substrate and the carrier fluid is allowed to evaporate. The ratio of air to ink and the distance from the substrate can be adjusted to allow the optimum amount of drying of the aerosol droplets before they impinge on the substrate surface. In this way the adhesion of the droplets to the substrate and the tendency of the ink to run or spread can be

controlled. Once dried the dried ink can have conductivity approaching that of a bare fibril mat depending on the level of any binder that may have been included in the ink formulation.

The compositions are prepared by dispersing oxidized fibrils in water first, then adding other additional ingredients if so desired.

The formation of thin fibril films with these compositions can be achieved by both printing and dip coating. Text and patterns have been printed with an Epson® ribbon printer. The surface resistivity of printed pattern was measured about  $3.5 \times 10^5 \Omega\text{-cm}$  (sample 4 in Table 1). The thickness of the pattern is in the range of few tens of nanometers, corresponding few layers of fibrils. Papers with  $\sim 2.5\text{mm}$  fibril coating on both sides have been prepared by dip-coating method. Measured surface resistivity for the coated paper is between 200-300  $\Omega\text{-cm}$ . Bulk resistivity of the fibril coating is  $\sim 5 \times 10^{-2} \Omega\text{-cm}$ , a number very close to that measured for a freestanding fibril mat. Furthermore, adhesion of fibril films to the paper is excellent due to the strong interaction between functional groups on the fibril surface and groups associated with cellulose paper.

**Table 1.**

**Composition and Properties of Fibril-Based Ink**

| Sample | Composition(%) |                  |    |      |      | V(cps) | t ( $\mu\text{m}$ ) | Resistivity                                |                               |
|--------|----------------|------------------|----|------|------|--------|---------------------|--|-------------------------------|
|        | Fibril         | H <sub>2</sub> O | EG | SS   | DIOP |        |                     | $\rho_{\text{sur}}$ ( $\Omega\text{-cm}$ ) | $\rho$ ( $\Omega\text{-cm}$ ) |
| 1      | 2              | 98               | —  | —    | —    | 0      | 2.5                 | 200-300                                    | $5 \times 10^{-2}$            |
| 2      | 4              | 96               | —  | —    | —    | 19.2   | —                   | —  | —                             |
| 3      | 2.5            | 77.5             | 20 | —    | —    | 0      | —                   | —  | —                             |
| 4      | 2.5            | 77.17            | 20 | 0.03 | 0.3  | 0      | —                   | $3.5 \times 10^5$                          | $5 \times 10^{-2}$            |

### **Modification of Carbon Nanotube Films**

The carbon nanotubes, or film, may be modified by chemical or mechanical treatment. The surface may be treated to introduce functional groups. Techniques that may be used include exposing the carbon nanotubes to electromagnetic radiation, ionizing radiation, plasmas or chemical reagents such as oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, and strong bases and /or combinations thereof. Of particular interest is plasma treatment.

### **Plasma Treatment of Nanotube Films**

Plasma treatment is carried out in order to alter the surface characteristics of the carbon fibrils, fibril structures and/or the matrix, which come in contact with the plasma during treatment; by this means the fibril composite treated can be functionalized or otherwise altered as desired. Once equipped with the teaching herein, one of ordinary skill in the art will be able to adapt and utilize well-known plasma treatment technology to the treatment of such composite materials. Thus, the treatment can be carried out in a suitable reaction vessel at suitable pressures and other conditions and for suitable duration, to generate the plasma, contact it with the composite material, and effect the desired kind and degree of modification. Plasmas such as those based on oxygen, hydrogen, ammonia, helium, or other chemically active or inert gases can be utilized.

Examples of other gases used to generate plasmas include, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfurhexafluoride, perfluoroethylene, fluoroform, difluorodichloromethane, bromo-trifluoromethane, chlorotrifluoromethane, and the like. Plasmas may be generated from a single gas or a mixture of two or more gases. It may be advantageous to expose a composite material to more than one type of plasma. It may also be advantageous to expose a composite material to a plasma multiple times in succession; the conditions used to

generate the plasma, the duration of such successive treatments and the duration of time between such successive treatments can also be varied to accomplish certain alterations in the material. It is also possible to treat the composite material, e.g., coat the material with a substance, wash the surface of the material, etc., between successive treatments.

Plasma treatment of a composite material may effect several changes. For example, a composite material comprising a polymer and a plurality of carbon fibrils dispersed therein can be exposed to plasma. Exposure to plasma may etch the polymer and expose carbon fibrils at the surface of the composite, thus increasing the surface area of exposed carbon fibrils, e.g., so that the surface area of the exposed fibrils is greater than the geometric surface area of the composite. Exposure to plasma may introduce chemical functional groups on the fibrils or the polymer.

Treatment can be carried out on individual fibrils as well as on fibril structures such as aggregates, mats, hard porous fibril structures, and even previously functionalized fibrils or fibril structures. Surface modification of fibrils can be accomplished by a wide variety of plasmas, including those based on F<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, He, N<sub>2</sub> and H<sub>2</sub>, other chemically active or inert gases, other combinations of one or more reactive and one or more inert gases or gases capable of plasma-induced polymerization such as methane, ethane or acetylene. Moreover, plasma treatment accomplishes this surface modification in a "dry" process as compared to conventional "wet" chemical techniques involving solutions, washing, evaporation, etc. For instance, it may be possible to conduct plasma treatment on fibrils dispersed in a gaseous environment.

Once equipped with the teachings herein, one of ordinary skill in the art will be able to practice the invention utilizing well-known plasma technology. The type of plasma used and length of time plasma is contacted with fibrils will vary depending upon the result sought. For instance, if oxidation of the fibrils' surface is sought, an O<sub>2</sub> plasma would be used, whereas an



ammonia plasma would be employed to introduce nitrogen-containing functional groups into fibril surfaces. Once in possession of the teachings herein, one skilled in the art would be able to select treatment times to effect the degree of alteration/functionalization desired.

More specifically, fibrils or fibril structures are plasma treated by placing the fibrils into a reaction vessel capable of containing plasmas. A plasma can, for instance, be generated by (1) lowering the pressure of the selected gas or gaseous mixture within the vessel to, for instance, 100 - 500 mTorr, and (2) exposing the low-pressure gas to a radio frequency which causes the plasma to form. Upon generation, the plasma is allowed to remain in contact with the fibrils or fibril structures for a predetermined period of time, typically in the range of approximately 10 minutes more or less depending on, for instance, sample size, reactor geometry, reactor power and/or plasma type, resulting in functionalized or otherwise surface-modified fibrils or fibril structures. Surface modifications can include preparation for subsequent functionalization.

Treatment of a carbon fibril or carbon fibril structure as indicated above results in a product having a modified surface and thus altered surface characteristics which are highly advantageous. The modifications can be a functionalization of the fibril or fibril structure such as chlorination, fluorination, etc., or a modification which makes the surface material receptive to subsequent functionalization, optionally by another technique or other chemical or physical modification as desired.

### **Chemical Treatments of Nanotube Films**

Chemical treatment can be also used. Acid treatments, particularly severe acids treatments, result in cutting the lengths of nanotubes, sharpening the ends of nanotubes, creating defects on the surface of nanotubes and introducing functional groups on the surface of nanotubes. Acid treated nanotubes are water dispersible, so chemical treatment offers advantages

for the formation of nanotube film electrodes. Functional groups can be mostly removed by thermal treatment. The process for doing this is disclosed in U.S. Patent No. 6,203,814. The Raman effect or titration can be used to measure the effect of the acid treatment. Raman can be used to measure the degree of structure imperfection after removing oxygen groups introduced during acid treatment. The effect of the treatment can be measured by electron spin resonance or simple titration as disclosed therein. See also, R. Khan et al. *Electron Delocalization in Amorphous Carbon by Ion Implantation*, 63 PHYSICAL REVIEW B 121201-1 (2001).

In metal vapor treatment procedures metal atoms can be introduced into nanotube films by heating films under vapor of a metal. For example, Cs atoms, which have been shown to enhance field emission, can be introduced into a nanotube film by placing the film in a vacuum chamber which has a Cs source held at 200 °C above (Vapor pressure of Cs at 373 °C is 10 mm Hg).

Chemical vapor transport methods can be used. Most metals vaporize at very high temperature. Metal atoms of these metals, such as Ga, can be introduced into nanotube films by chemical vapor transport. The nanotube film is placed in an evacuated glass tube; at one end, a metal particle is placed at the other end. A chemical vapor transport agent, such as Cl<sub>2</sub>, I<sub>2</sub>, Br<sub>2</sub> and HCl is also included. The tube is placed into a three-zone furnace. The temperature of nanotube is held lower than that of the metal, so that metal atoms are transported to the nanotube films by the transport agent.

Chemical sorption followed by heat treatment can be used. Metal atoms can be introduced into nanotube films by first absorbing a metal compound like metal halides or organometallic compounds on the surface of the nanotube films, followed by heating then under inert gas atmosphere to convert metal halides or organometallic compounds to metal atoms. For

example Ge atoms may be introduced into a nanotube film by absorbing  $\text{GeBr}_2$  on the surface of nanotubes from a  $\text{GeBr}_2$  alcohol solution, then heating the nanotube film between 200 and 400 °C to decompose  $\text{GeBr}_2$ .

Functionalization of nanotubes by chemical sorption can be used, some molecules, like metal phthalocyanines may have the effect of lowering work function of nanotubes and lead to an enhancement of field emission when absorbed on the surface of nanotubes. Absorption can be carried out by placing a nanotube film electrode in a phthalocyanine, porphyrin or metalloporphyrin solution; this procedure is disclosed in U.S. Patent No. 6,203,814. The functionalization is carried out by phthalocyanines, metalloporphyrins, porphyrins or other organometallics.

The treatment can also include annealing the film after functionalization. The annealing temperature can be carried out between 200 and 900 degrees Celsius in inert gas or under 360 degrees Celsius in air.

#### **Ion Bombardment of Carbon Nanotube Films**

The carbon nanotube films, are treated by ion bombardment before use in a field emission device or field emitting cathode.

The settings used to bombard the carbon nanotubes were as follows:

energy: 30 keV. Other ranges appropriate for the present invention can be from about 5eV to about 1MeV, e.g., 10-50 keV.

ion: Ga. Although Ga was used as the ion, any type of ion can be used. Other types of ions, for example, include H, He, Ar, C, O, and Xe.

spot size: defocused, 500 nm. Other ranges appropriate for the present invention include from about 1 nm to about 1 micron. Appropriate spot size can also be based on desired resolution and dose.

scan area: 760 microns x 946 microns Rasterscanned for about twenty seconds. Any appropriate scan area will suffice.

dose:  $2 \times 10^{14} / \text{cm}^2$  ranges include from about  $10^2 / \text{cm}^2$  to about  $10^{20} / \text{cm}^2$

#### **Additional Methods for Treatments of Nanotube Films**

Other energetic beams/sources, including atomic beams, electron beams, neutron beams, molecular beams, lasers, plasmas, UV light, x-ray and gamma rays can be used to treat nanotube films instead of ion bombardment. Mechanical treatment resulting in mechanical disruption, for example, ball milling can be used.

Other characteristics of carbon nanotubes can be modified by the above treatments. For example, the treatments can remove surface oxygen, remove insulating oxidation residues, generate edges, points, and singularities, recrystallize the tubes, generate non-tube carbon nanoparticles. A treatment can also be used to clean the carbon nanotubes, for example cleaning to remove the insulation coating generated by oxidation and cleaning to remove oxygen.

#### **Characterization of the Treated Film**

By viewing samples in a SEM it is possible to detect irradiated areas by contrast change, i.e., dark image. Figure 12 illustrates scanning electron microscope views of carbon nanotubes on aluminum.

Figure 7 schematically illustrates an apparatus used to make the emission measurements. Figure 7 illustrates the top view, Figure 7a, and side views, Figure 7b. Figure 7a shows a 6 mm x 6 mm phosphor on indium tin oxide (ITO). In Figure 7b, the phosphor is shown to be spaced

from the patterned carbon nanotubes by a distance of 125  $\mu\text{m}$ . The entire system is evacuated with a vacuum of  $5 \times 10^{-9}$  Torr in the emission chamber.

The degree of improvement achieved by ion beam treatment are summarized in Table 2.

**Table 2**

|                   | Untreated CNT Cathode | Treated / Modified CNT Cathode |
|-------------------|-----------------------|--------------------------------|
| Threshold voltage | 350 Volts             | 140 Volts                      |
| Threshold Field   | 2.8 V / $\mu\text{m}$ | 1.1 V / $\mu\text{m}$          |
| Emission current  | see figure 8          | 6 times increase               |

The ion bombardment achieves a reduction in work voltage, increases emission current and increases the number of emission sites. With reference to Figure 8, it is seen that the turn-on voltage was reduced substantially as the result of ion beam treatment.

Figure 9 is a Fowler-Nordheim (F-N) plot. The shape of the curves provides the theoretical proof of FE. Shifting the curve toward the right side - toward lower voltage - indicates an increased number of emission sites.

Similar improvements can be obtained by treating the carbon nanotubes with ultra-violet light, laser beam and plasma.

## **EXAMPLE II**

### **Emission Characteristics of Ion-Beam-Treated Nanotube Films**

Carbon nanotube films fabricated by electrophoresis on an aluminum layer deposited on a glass have been locally irradiated with focused ion beams. A diode structure with a distance of 125  $\mu\text{m}$  between cathodes and anodes was used for emission measurement. A maximum emission current of 375 microamps with a turn-on voltage of 2.8 V/ $\mu\text{m}$  for carbon nanotube

emitters was found to decrease by focused ion beam irradiation to 1.1 V /  $\mu\text{m}$  with increase in emission current by a factor of six.

The current range that was used in the test was in the low range with an anode voltage of about 400 to 500 volts, close to the turn-on (threshold) voltage for field emission. The change was from 0.05 to about 0.18 microamps to more than 0.9 microamps with a drastic change in the F-N plot of Figure 9.

The physical and chemical effects of ion bombardment on carbon nanotubes are not entirely known. While not wishing to be bound to any particular theory, it may be that the effect of the ion bombardment is the creation of surface sites which enhance field emission. It is believed that the treatment 1) cuts lengths of nanotubes, in particular, if high energy beams are used, hence generating more ends; 2) implants ions, like Ga ions, into the nanotube film, the ions being inside a single tube and outside tubes; 3) saturates dangling bonds with hydrogen (where a hydrogen ion beam/plasma is used), resulting in hydrogenated surface; 4) cleans the surface of nanotubes by removing contaminants, such as binder residue and oxygenated groups; 5) generates localized and delocalized regions along the nanotube axis by creating pits and carbon nanoparticles and recrystallizing amorphous carbons on the surface of nanotubes, and disrupting carbon layers, leading to an increasing in emission sites; 6) improves electric contacts between nanotubes.

The surface sites generated by ion bombardment can be defects, which are carbon atoms at edges, carbon atoms associated with other atoms, like a hydrogen atom, and an implanted Ga atom, and carbon atoms with a  $\text{sp}^3$  configuration or configurations between  $\text{sp}^2$  and  $\text{sp}^3$ . The defects can be at the ends (exposed) of a nanotube, and on the surface of a single nanotube associated with a nanoparticle, a pit and a disrupted carbon layer.

**Construction of a Field Emission Display Device Using  
Treated Carbon Nanotube Cathodes**

Generally, field emission display devices are based on the emission of electrons in a vacuum. Emitter tips emit electrons that are accelerated in a strong electric field. The electrons ultimately collide with fluorescent materials that emit light. The advantages of this type of display over other types, such as cathode ray tubes, are that they are very thin and light and yield high brightness and resolution. Processes for constructing these devices are disclosed in EP No. 1,073,090 A2.

Figure 1 shows an exemplary embodiment of a field emission display device using an treated carbon nanotube cathode. The field emission display 1000 includes, for example, a first substrate 1010, first metal film 1020, a conductive high polymer film 1030, a dielectric film 1040, a second metal film 1050, a spacer 1060, a transparent electrode 1070, a second substrate 1080, and emitter tips, the treated carbon nanotube cathode, 1090.

The substrate 1010 is, for example, made of glass quartz, silicon, or alumina ( $\text{Al}_2\text{O}_3$ ). Other substrates include silica, platinum, iron and its alloys, cobalt and its alloys, nickel and its alloys, and ceramics.

The first metal film 1020 functions as the cathode and is, for example, made of chrome, titanium, tungsten, or aluminum. The first metal film 1020 has a thickness from about 0.2 to about 0.5  $\mu\text{m}$ .

On the first metal film 1020 is, for example, the dielectric film 1040. The dielectric film 1040 has a thickness from about one to about five  $\mu\text{m}$ .

On the dielectric film 1040 is the second metal film 1050. The second metal film 1050 functions as a gate electrode and is made from, for example, chrome, titanium, or palladium. The thickness of the second metal film is from about 0.2 to 0.5  $\mu\text{m}$ . The second metal film 1050

can also be patterned, for example, by using a photoresist film that has a thickness from about 1.5 to about 2.0  $\mu\text{m}$ . The photoresist film is later developed forming a photoresist pattern. The accelerating gate electrode should be in close proximity to the emitting source approximately one to ten  $\mu\text{m}$ .

Both the first metal film 1020 and the dielectric film 1040 have a plurality of fine holes. The holes have, for example, a diameter of 0.5 to 10.0  $\mu\text{m}$  and are separated from each other by about 2.0 to about 15.0  $\mu\text{m}$ .

Formed within the fine holes of the dielectric film 1040 and the second film 1050, is the conductive high polymer film 1030. The conductive high polymer film 1030 can be, for example, made from carbon adhesive or silver adhesive. To attach the conductive high polymer film 1030 to the first metal film 1020, the conductive high polymer film 1030 is liquefied by heating and poured to fill approximately one-third of each of the fine holes.

Arranged vertically or horizontally within the conductive high polymer film 1030 are carbon nanotubes used as emitter tips 1090. The emitter tips 1090 are made from the ion bombarded carbon nanotubes discussed previously. These emitter tips 1090 can obtain a great amount of emission current at a low operating voltage, for example, about 1.5 V/ $\mu\text{m}$ . The range can be from about 0.1 to about 2.0 V/ $\mu\text{m}$ , e.g., about 0.8 V/ $\mu\text{m}$  to about 1.5V/ $\mu\text{m}$ .

Above the second metal film 1050 is the spacer 1060. The spacer 1060 is installed to about 100 to about 700  $\mu\text{m}$ . on the second metal film 1050.

The transparent electrode 1070 is on top of the spacer 1060. The transparent electrode 1060 functions as an anode and is made of a conducting oxide, such as indium oxide, indium tin oxide, tin oxide, copper oxide, or zinc oxide.



The second substrate 1080 is on the transparent electrode 1070 and can be made of glass. Fluorescent material, attached to the transparent electrode 1070, emits red, blue, or green light when electrons contact it.

The emitter tips 1090 are made of the ion bombarded carbon nanotubes. The geometrical features of the emitter tips 1090 should be small. For example, the diameters of each emitter tip 1090 should be as small as 1.3 nm. The average height of the nanotubes is from about 0.1 to about 1000  $\mu\text{m}$ , preferably between 0.1 to about 100  $\mu\text{m}$ . The average diameter is between 1.3 to 200 nm depending on whether the nanotubes are single walled or multi-walled.

More than  $10^4$  emitting tips are needed per pixel of  $100 \times 100 \mu\text{m}^2$  assuming 50% of nanotube density with a tubule diameter of about 10 to about 100 nanometers. The emitter density is preferably at  $1 / \mu\text{m}^2$ , in particularly at least  $10 / \mu\text{m}^2$ . The entire field emission display 1000 is evacuated.

In Figure 2, a field emission display 2000 is shown. The field emission display 2000, includes, for example, a baseplate 2010, a spaced-apart phosphor coated faceplate 2020, and an electron emitter array 2030 positioned on the baseplate 2010 for emitting electrons that collide with the phosphor causing illumination. The components of the field emission display 2000 are in a vacuum. The electron emitter array (cathode) 2030 is composed of treated carbon nanotubes that can have either an orientation parallel, perpendicular, or any angle between zero and ninety degrees to the baseplate 2010. (See PCT/US 99/13648 - Free Standing and Aligned Carbon Nanotubes and Synthesis thereof).

Figure 3 shows yet another embodiment of the field emission device. The device 3000, has, for example, a substrate 3010, a porous top layer 3020, a catalyst material 3030, and bundles of treated carbon nanotubes 3040 as the cathode.

The substrate 3010 and the porous top layer 3020 can be made of, for example, silicon. The catalyst material 3030 can be a thin film of iron oxide that is formed in a particular pattern. The carbon nanotube bundles 3040 serve as the cathode. The bundles 3040 are oriented substantially perpendicular to the substrate 3010. Alternatively, the bundles 3040 can also be oriented substantially parallel to the substrate 3010.

The carbon nanotube bundles 3040 may be about 10-250  $\mu\text{m}$  wide, and up to or greater than three hundred  $\mu\text{m}$  in height. The bundles 3040 are of the same size and shape as the patterns of catalyst material 3030, for example. The nanotube bundles 3040 can have flat tops or bowl-shaped tops as shown in the figure. The sharp edges of the nanotube bundles 3040 function as field emission regions. Each bundle 3040 provides the field emission for a single pixel in a flat panel display.

The device is evacuated to from about  $10^{-3}$  Torr to about  $10^{-9}$  Torr, e.g., from about  $10^{-7}$  Torr to about  $10^{-8}$  Torr.

The calculation of any electrical field within the device 3000 is made by taking the applied voltage and dividing it by the distance from the emitter tips to the anode. See (PCT appln. PCT/US99/26332)

Figure 4 shows another embodiment of a flat panel field emission display 4000. The display 4000, for example, includes cathode 4010 that contains a plurality of treated carbon nanotube emitting tips 4020 and an anode 4030. The anode 4030 further includes an anode conductor 4040 and a phosphor layer 4050. Between the cathode 4010 and the anode 4030 is a perforated conductive gate electrode 4060. Between the gate electrode 4060 and the cathode 4010 is an insulating layer 4070. The space between the anode 4030 and the carbon nanotube emitting tips are sealed and evacuated. The voltage is supplied by a power supply. The

electrons emitted from the emitting tips 4020 are accelerated by the gate electrode 4060, and move toward the anode conductor layer 4080 which is a transparent conductor such as indium-tin oxide. The gate electrode 4060 should be within 10  $\mu\text{m}$  of the emitting tips 4020. As the emitted electrons hit the phosphor layer 4050, light is given off. (see, EP 1,022,763 A1). The colors of the emitted light depend on the phosphors that are used. For example Zn:Scu, Al for green,  $\text{Y}_2\text{O}_3\text{:Eu}$  for Red, and ZnS:Ag for blue.

The cathodes and anodes can be referred to as sources and drains respectively.

### **Operation of a Field Emission Device**

To operate the field emission display device, the treated carbon nanotube cathode is held at a negative potential relative to the anode. As a result of this potential difference, electrons are emitted from the emitter tips and travel to the anode. The gate electrode can be used to accelerate the emitted electrons.

### **Field Emission Display Devices**

Using the ion bombarded carbon nanotube cathode, various devices can be created, such as a field emitter array. An array can include a single nanotube, a single bundle, or many carbon nanotubes and field emission display, e.g., a flat panel television. The treated carbon nanotube can constitute the array. Figure 10 is an illustration of a classical field emitter.

Table 3 shows example characteristics of a field emitter display

**Table 3**

| emission type                  | low & high voltage |
|--------------------------------|--------------------|
| brightness ( $\text{cd/m}^2$ ) | 150, 600           |
| viewing angle (degrees)        | 160                |
| emission efficiency (lm        | 10-15              |
| response time                  | 10-30              |
| contrast ratio                 | > 100:1            |
| number of colors               | 16 million         |
| number of pixels               | 640/480            |

|                           |          |
|---------------------------|----------|
| resolution (mm pitch)     | 0.31     |
| power consumption (W)     | 2        |
| max screen size (cm)      | 26.4     |
| panel thickness (mm)      | 10       |
| operating temp range (°C) | -5 to 85 |

The advantages of field emission display over other types of displays such as cathode ray tubes include: high brightness, peak brightness, full viewing angle, high emission efficiency, high dynamic range, fast response time and low power consumption.

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PCT Appln. PCT/SE00/015221 - A Light Source, and a Field Emission Cathode

#### *Other Uses*

PCT Appln. PCT/US99/13648 - Free-Standing and Aligned Carbon Nanotubes and Synthesis Thereof (scanning electron microscope, alkali metal batteries, electromagnetic interference shield, and microelectrodes).

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We claim:

1. A field emission device comprising:

a cathode; and

an anode spaced from the cathode,

wherein said cathode includes emitters comprising carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment.

2. The field emission device of claim 1, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layers concentric with their cylindrical axes, said carbon fibrils being substantially free of pyrolytically deposited carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

3. The field emission device of claim 1, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates.

4. The field emission device of claim 1, wherein said nanotubes have a morphology resembling a fishbone.

5. The field emission device of claim 1, wherein said nanotubes are single wall nanotubes.

6. The field emission device of claim 1, wherein said nanotubes are in the form of a film or mat.

7. The field emission device of claim 1, wherein said nanotubes have been treated with an ion beam.

8. The field emission device of claim 1, wherein said nanotubes have been treated with a gallium ion beam.



9. The field emission device of claim 1, wherein said nanotubes have been treated with a beam of ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

10. The field emission device of claim 1, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport and chemical sorption.

11. The field emission device of claim 1, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

12. The field emission device of claim 1, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

13. The field emission device of claim 1 wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

14. The field emission device of claim 1 wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

15. The field emission device of claim 1, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

16. The field emission device of claim 1, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

17. The field emission device of claim 16, wherein said functional groups have been introduced by chemical sorption.

18. The field emission device of claim 1, wherein said treatment comprises heating the carbon nanotubes in the presence of metal vapor.

19. The field emission device of claim 1, wherein said treatment comprises chemisorption followed by heat treatment.

20. The field emission device of claim 1, wherein said treatment includes annealing said nanotubes.

21. The field emission device of claim 1, wherein said cathode further includes a binder.

22. The field emission device of claim 21, wherein said binder is a conductive carbon paste, conductive metal paste or carbonizable polymer.

23. A process for treating carbon nanotubes comprising the step of bombarding carbon nanotubes with ions.

24. The process for treating carbon nanotubes of claim 23, wherein the nanotubes are bombarded with gallium ions.

25. The process of treating carbon nanotubes of claim 23, wherein the nanotubes are bombarded with ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

26. Carbon nanotubes formed by the process of claim 23.

27. A field emission cathode comprising carbon nanotubes, wherein said nanotubes have been subjected to energy, plasma, chemical, or mechanical treatment.

28. The field emission cathode of claim 27, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layers concentric with their cylindrical

axes, said carbon fibrils being substantially free of pyrolytically deposited carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

29. The field emission cathode of claim 27, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates or bird nest aggregates.

30. The field emission cathode of claim 27, wherein said nanotubes have a morphology resembling a fishbone.

31. The field emission cathode of claim 27 wherein said nanotubes are single wall nanotubes.

32. The field emission cathode of claim 27, wherein said nanotubes are in the form of a film or mat.

33. The field emission cathode of claim 27, wherein said nanotubes have been treated with an ion beam.

34. The field emission cathode of claim 27, wherein said nanotubes have been treated with a gallium ion beam.

35. The field emission cathode of claim 27, wherein said nanotubes have been treated with a beam of ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

36. The field emission cathode of claim 27, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

37. The field emission cathode of claim 27, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

38. The field emission cathode of claim 27, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

39. The field emission cathode of claim 27, wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

40. The field emission cathode of claim 27, wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

41. The field emission cathode of claim 27, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

42. The field emission cathode of claim 27, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

43. The field emission cathode of claim 42, wherein said functional groups have been introduced by chemical sorption.

44. The field emission cathode of claim 27, wherein said treatment comprises heating the carbon nanotubes in the presence of metal vapor.

45. The field emission cathode of claim 27, wherein said treatment comprises chemisorption followed by heat treatment.

46. The field emission cathode of claim 27, wherein said treatment includes annealing said nanotubes.

47. The field emission cathode of claim 27, wherein said cathode further includes a binder.

48. The field emission cathode of claim 47, wherein said binder is a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

49. The field emission cathode of claim 27, wherein the nanotubes are deposited onto a substrate.

50. A method for making a field emission cathode comprising the steps of:

dispersing carbon nanotubes into a liquid vehicle to form a solution;

forming an electrophoresis bath, said bath including an anode and a cathode immersed therein;

applying a voltage to said anode and said cathode, thereby causing said carbon nanotubes to deposit onto said cathode;

removing said cathode from said bath; and

subjecting the nanotubes deposited on said cathode to an energy, plasma, chemical, or mechanical treatment.

51. The method for making a field emission cathode of claim 50, wherein said nanotubes are substantially cylindrical carbon fibrils having one or more graphitic layer concentric with their cylindrical axes, said carbon fibrils being substantially free of pyrolytically deposited

carbon overcoat, having a substantially uniform diameter between 1 nm and 100 nm and having a length to diameter ratio greater than 5.

52. The method for making a field emission cathode of claim 50, wherein said nanotubes are in the form of aggregates selected from the group consisting of cotton candy aggregates or bird nest aggregates.

53. The field emission display device of claim 50, wherein said nanotubes have a morphology resembling a fishbone.

54. The method of making a field emission cathode of claim 50, wherein said nanotubes are single wall nanotubes.

55. The method of making a field emission cathode of claim 50, wherein said nanotubes are in the form of a film or mat.

56. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with ions.

57. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with a gallium ions.

58. The method for making a field emission cathode of claim 50, wherein said cathode is bombarded with ions selected from the group consisting of hydrogen, helium, argon, carbon, oxygen, and xenon ions.

59. The method for making a field emission cathode of claim 50, wherein said chemical treatment is selected from the group consisting of acid treatment, metal vapor treatment, chemical vapor transport, and chemical sorption.

60. The method for making a field emission cathode of claim 50, wherein said chemical treatment is performed with chemical reagents selected from the group consisting of oxidizing

agents, electrophiles, nucleophiles, reducing agents, strong acids, strong bases and mixtures thereof.

61. The method for making a field emission cathode of claim 50, wherein said chemical treatment is performed with phthalocyanines or porphyrins.

62. The method for making a field emission cathode of claim 50, wherein said energy treatment is performed with an energy source selected from a group consisting of electromagnetic radiation, ionizing radiation, atomic beams, electron beams, ultraviolet light, microwave radiation, gamma ray, x-ray, neutron beam, molecular beams and laser beam.

63. The method for making a field emission cathode of claim 50, wherein said plasma treatment is performed with a plasma selected from a group consisting of oxygen, hydrogen, ammonia, helium, argon, water, nitrogen, ethylene, carbon tetrafluoride, sulfur hexafluoride, perfluoroethylene, fluoroform, difluoro-dichloromethane, bromo-trifluoromethane, chlorotrifluoromethane and mixtures thereof.

64. The method for making a field emission cathode of claim 50, wherein said treatment results in the introduction of metal atoms onto the carbon nanotubes.

65. The method for making a field emission cathode of claim 50, wherein said treatment results in the introduction of functional groups onto the carbon nanotubes.

66. The method for making a field emission cathode of claim 65, wherein said functional groups have been introduced by chemical sorption.

67. The method for making a field emission cathode of claim 50, wherein said treatment comprises heating said cathode in the presence of metal vapor.

68. The method for making a field emission cathode of claim 50, wherein said treatment comprises chemisorption followed by heat treatment.

69. The method for making a field emission cathode of claim 50, wherein said treatment includes annealing said nanotubes.

70. The method for making a field emission cathode of claim 50, further comprising the step of adding a binder to said solution before applying said voltage.

71. The method for making a field emission cathode of claim 70, wherein said binder is a conductive carbon paste, a conductive metal paste or a carbonizable polymer.

72. A field emission display device comprising:

- a cathode including carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment;
- an insulating layer on said cathode;
- a gate electrode on said insulating layer;
- an anode spaced from said cathode, said anode comprising a phosphor layer, an anode conducting layer, and a transparent insulating substrate; and
- a power supply.

73. A method for making a field emission cathode comprising the steps of:

- screen printing an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes in as-made form or which have been subjected to energy, plasma, chemical, or mechanical treatment; and
- evaporating said carrier liquid.

74. A method for making a field emission cathode comprising the steps of:

- ink jet printing an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes which have been in as-made form or which have been subjected to energy, plasma, chemical, or mechanical treatment; and



evaporating said carrier liquid.

75. A method for making a field emission cathode comprising the steps of:

spray painting an ink through a stencil onto a substrate, said ink comprising a carrier liquid and carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment; and

evaporating said carrier liquid.

76. A method for making a field emission cathode comprising the steps of:

screen printing, ink-jet printing or spray painting an ink onto a substrate, said ink comprising a carrier liquid and carbon nanotubes in as-made form; and subjecting said screen printed nanotubes to an energy, plasma, chemical or mechanical treatment.

77. A field emission cathode made by the method of claim 107.

78. A field emission display device comprising:

a baseplate;

an electron emitter array, said array including carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment;

a gate on said baseplate;

a phosphor coated faceplate spaced from said gate;

a faceplate on said phosphor coated faceplate; and

a power supply.

79. A field emission device comprising:

a substrate,

a porous top layer on said substrate,

a catalyst material on said layer; and

a cathode on said catalyst material, said cathode including a bundle of carbon nanotubes which have been subjected to energy, plasma, chemical, or mechanical treatment.

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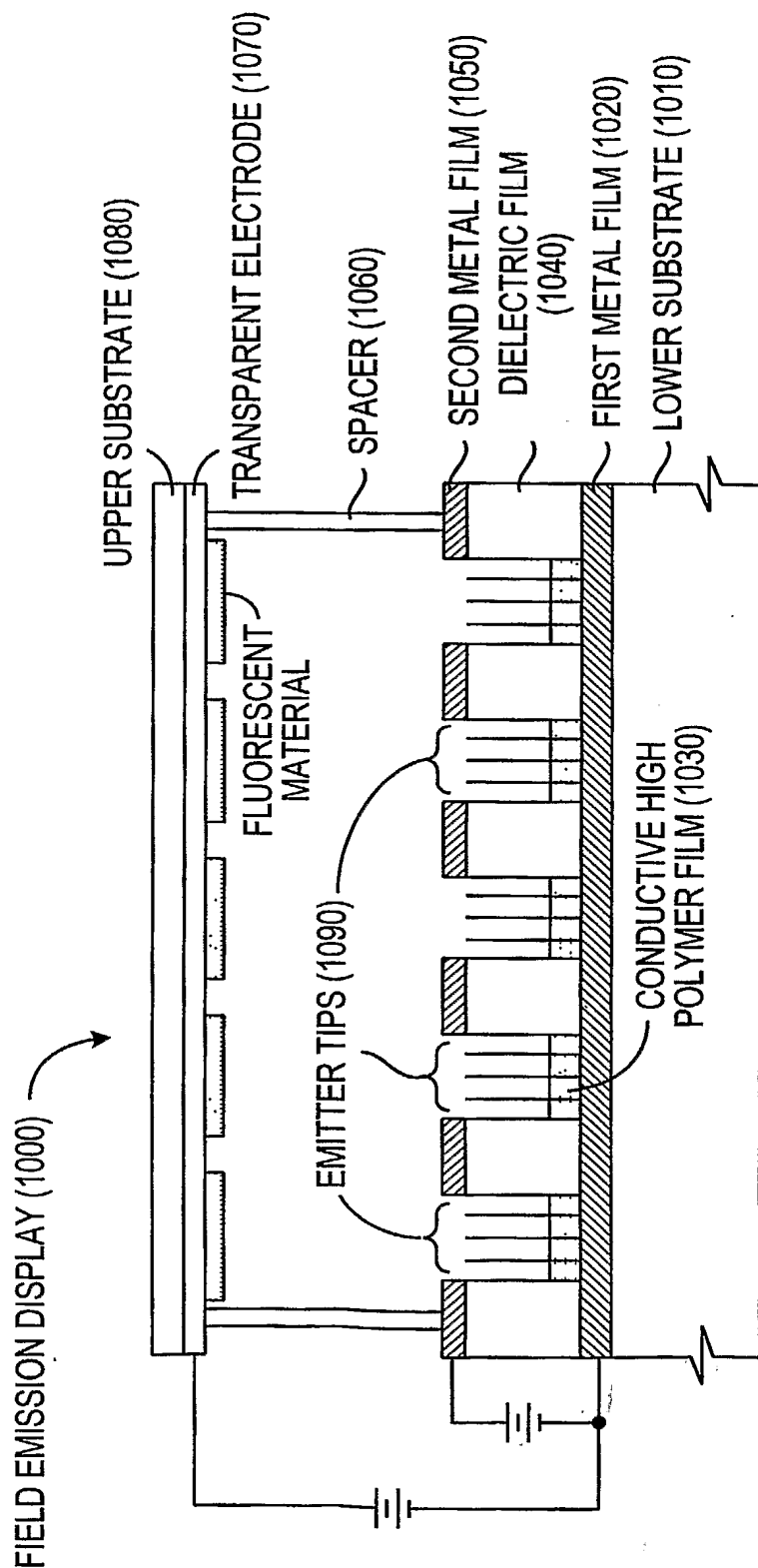


FIG. 1

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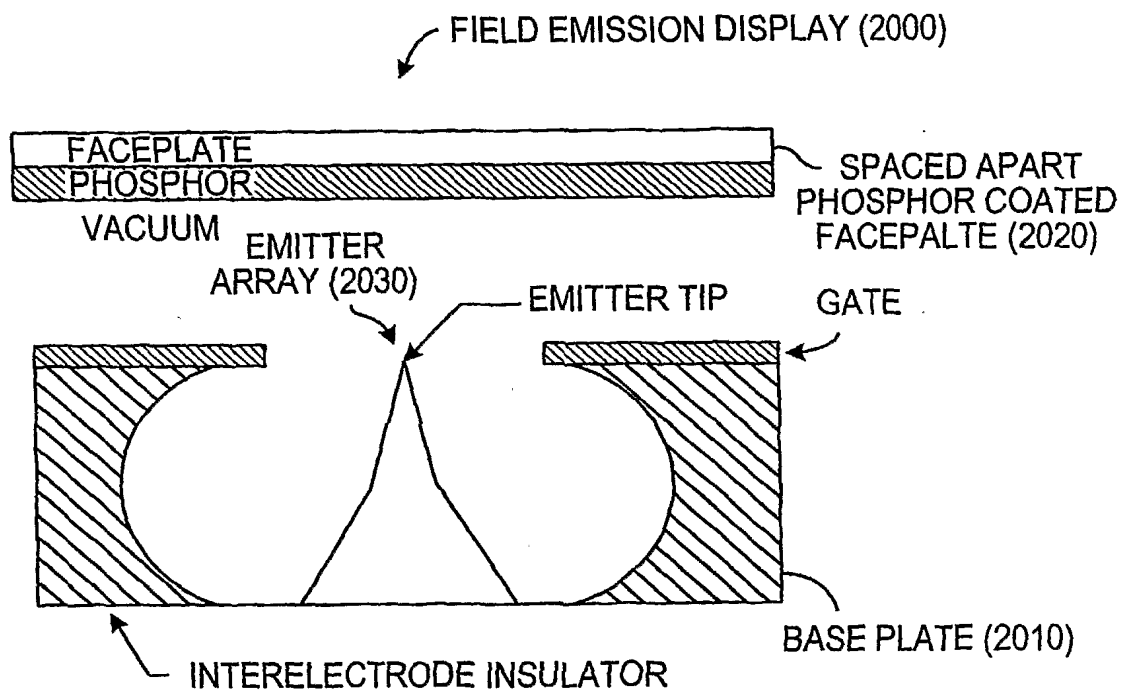


FIG. 2

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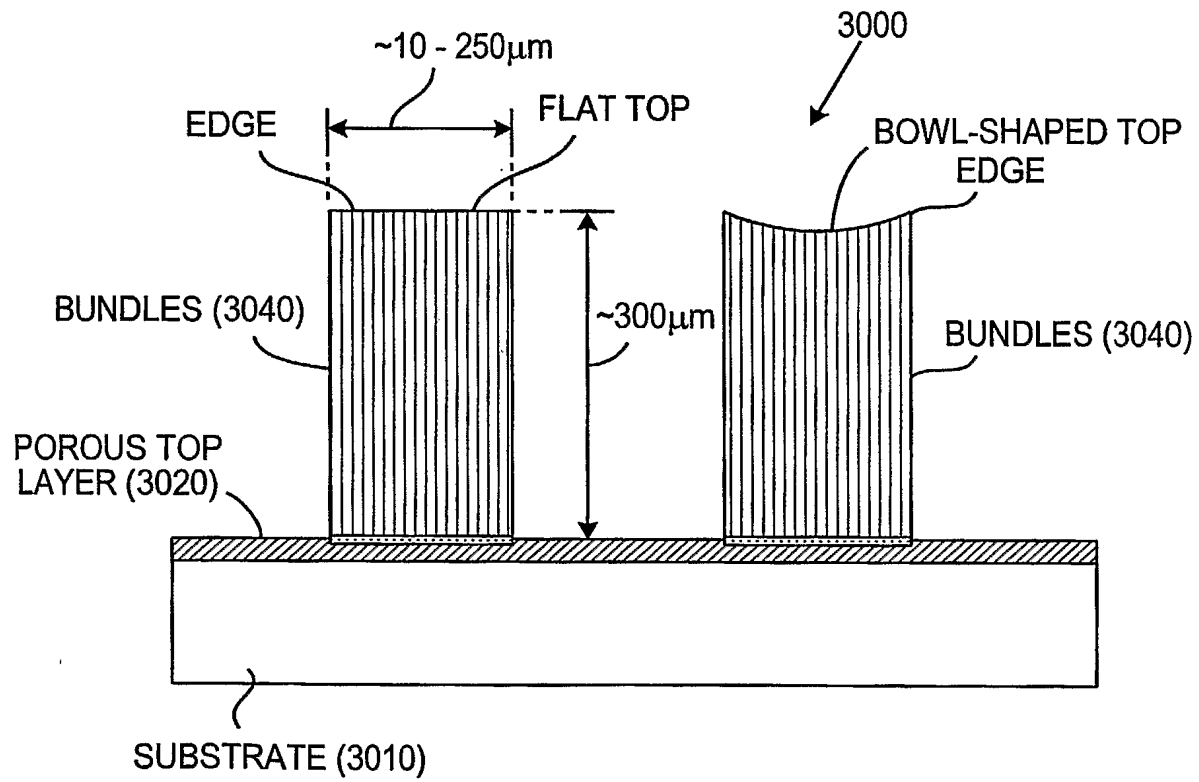


FIG. 3

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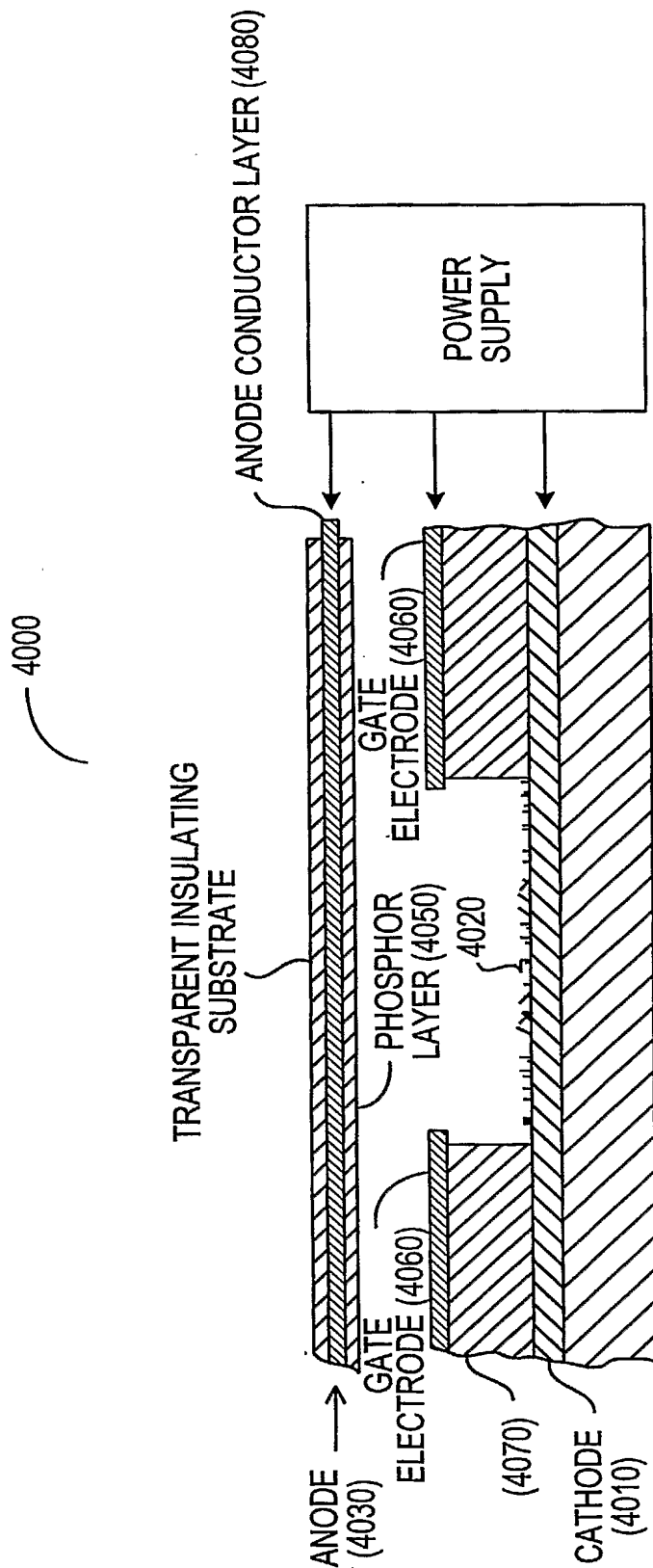


FIG. 4

# ELECTROPHORESIS / DEPOSITION

SOLUTION

CNT 0.44 g

IPA 150 ml

ELECTRODE

Al (9 mm x 9 mm) x 3

VOLTAGE

DC 100 V

CURRENT

3.8 mA

TIME 30 min

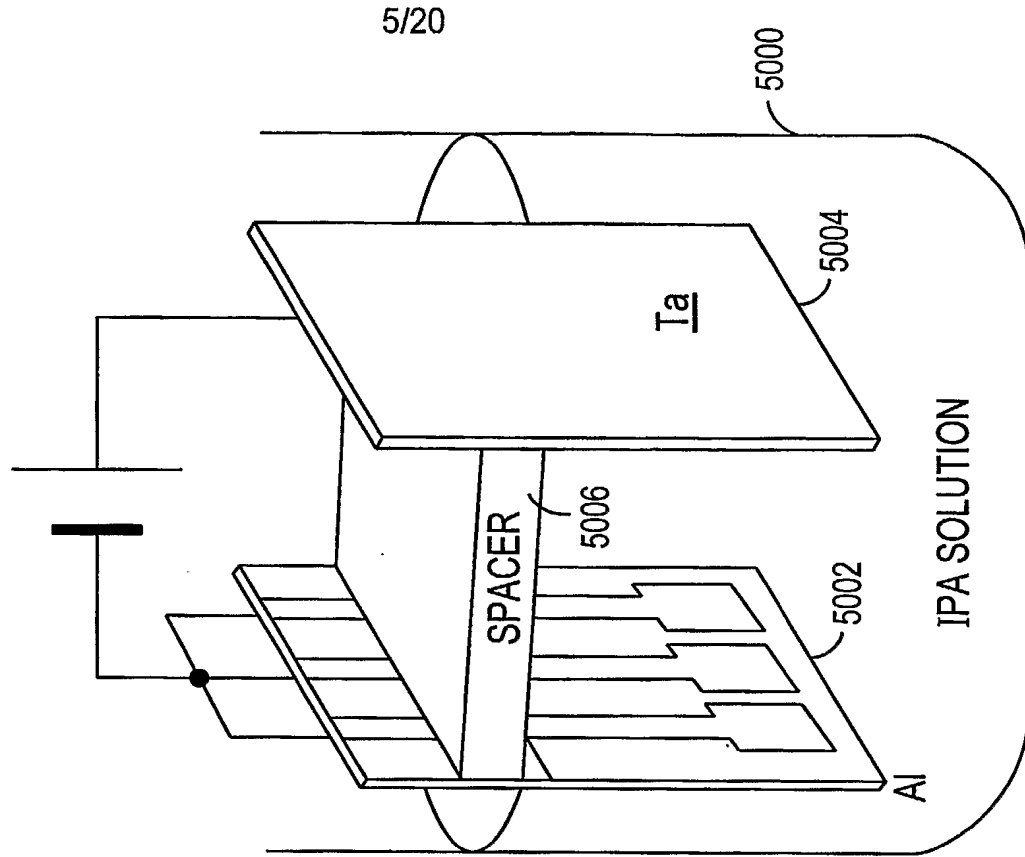
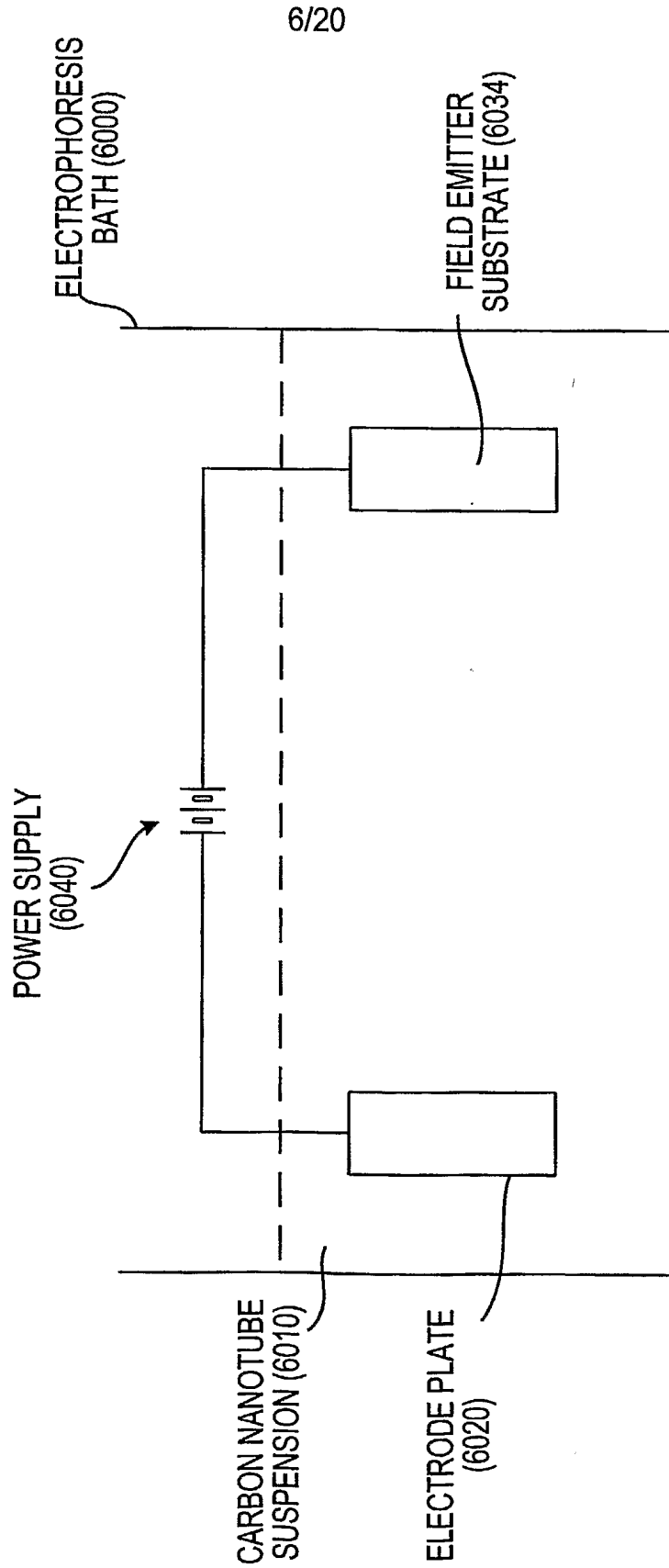


FIG. 5

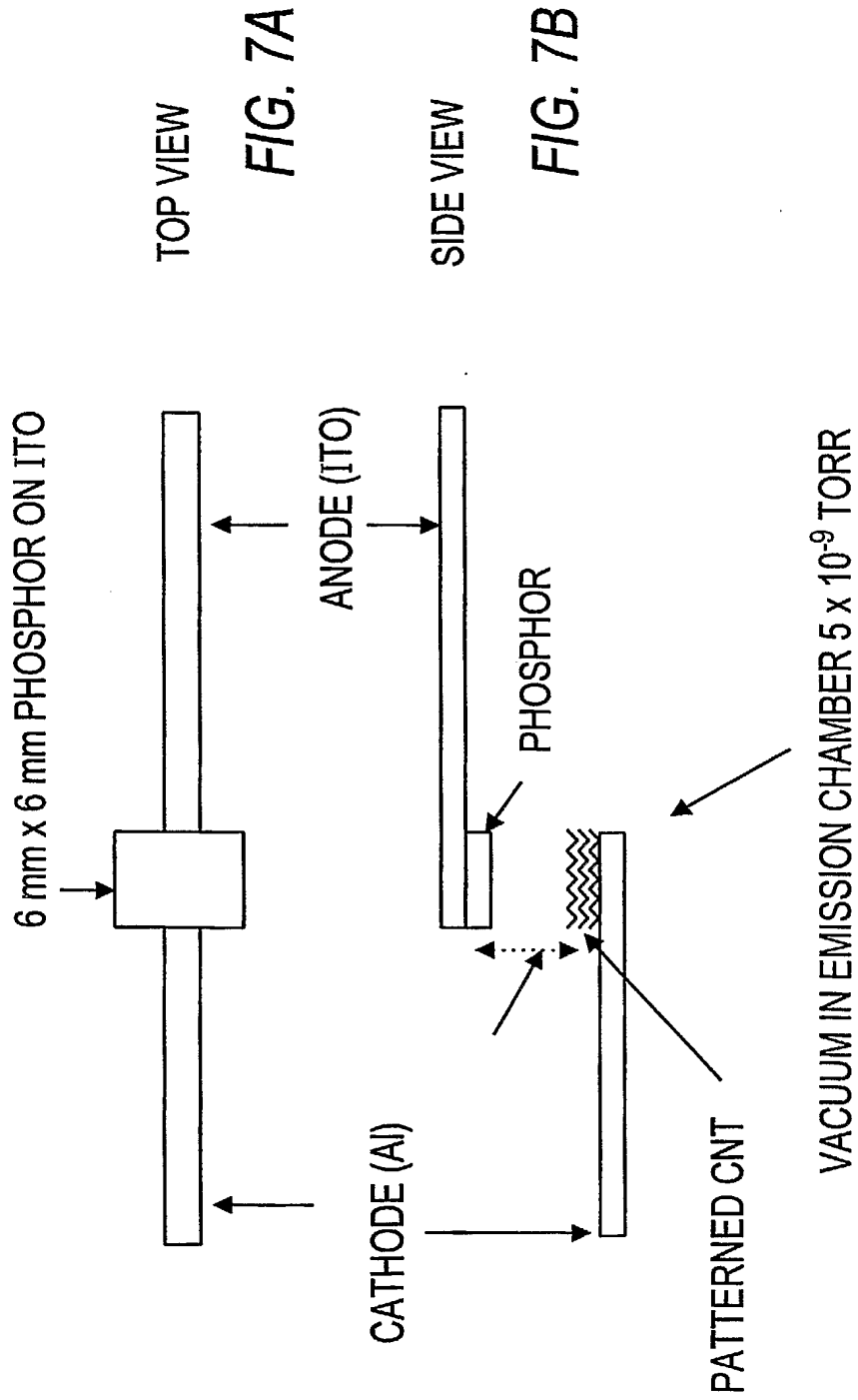
FIG. 6





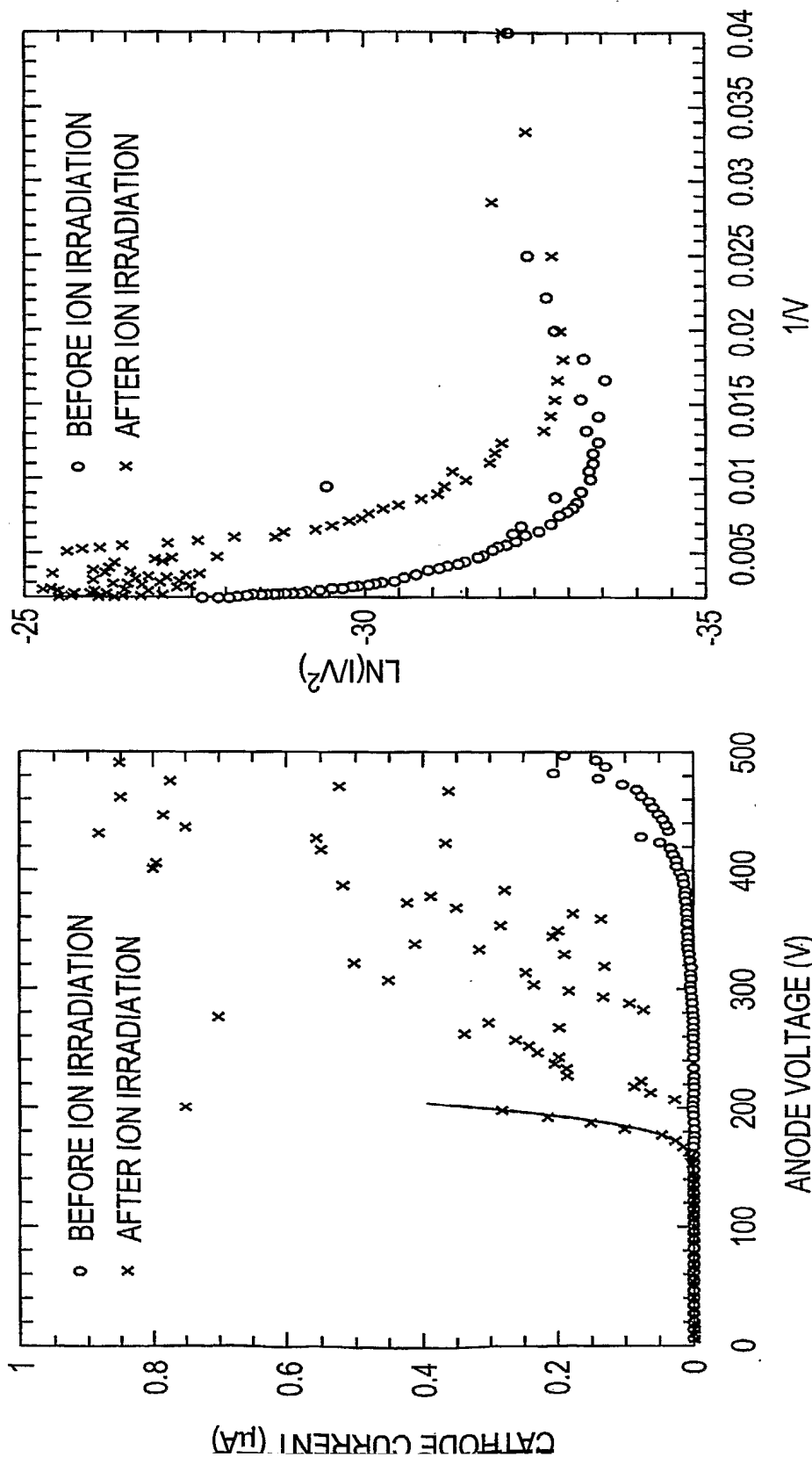
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SCHEMATIC OF EMISSION MEASUREMENT



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EMISSION CHARACTERISTICS  
BEFORE AND AFTER ION IRRADIATION



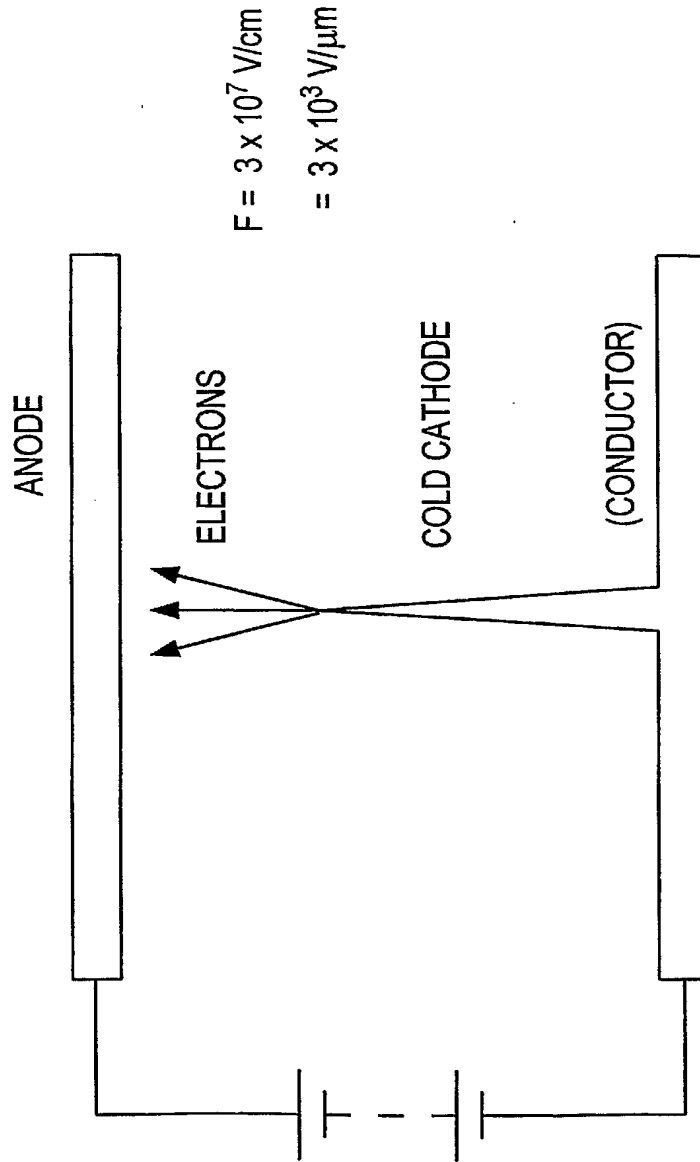
F-N PLOT  
FIG. 9

I-V CHARACTERISTICS

FIG. 8

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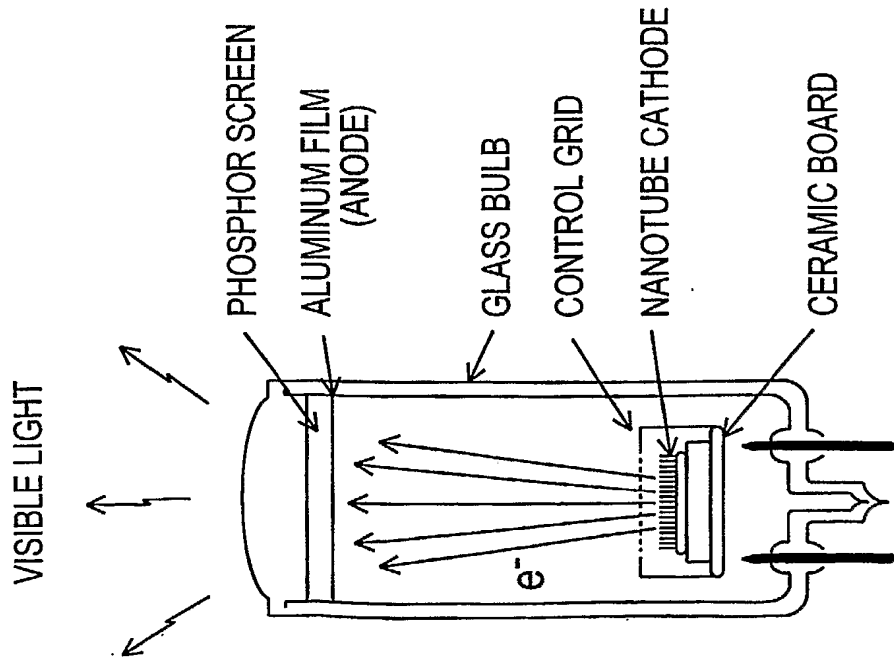
# CLASSICAL FIELD EMITTER



OBSERVATION BY R.W. WOOD (1897)  
 THEORY BY FOWLER AND NORDHEIM (1928)

FIG. 10

# FED WITH CARBON NANO TUBES



SUBSTITUTE SHEET (RULE 26)

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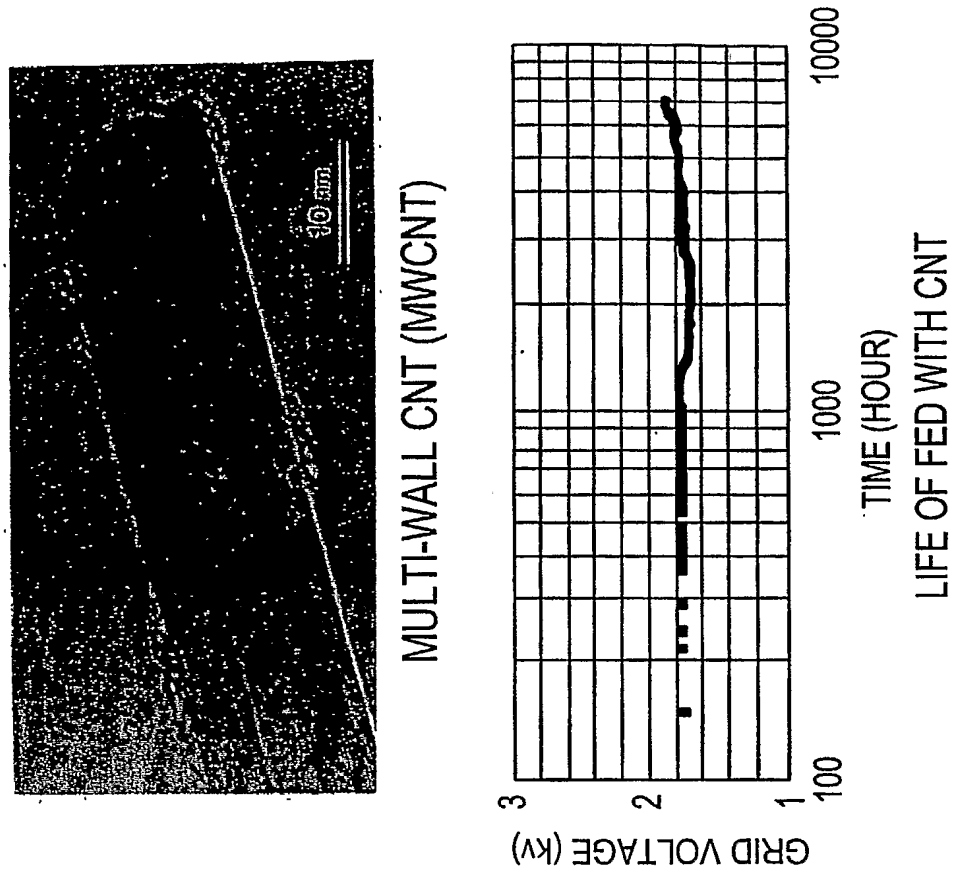
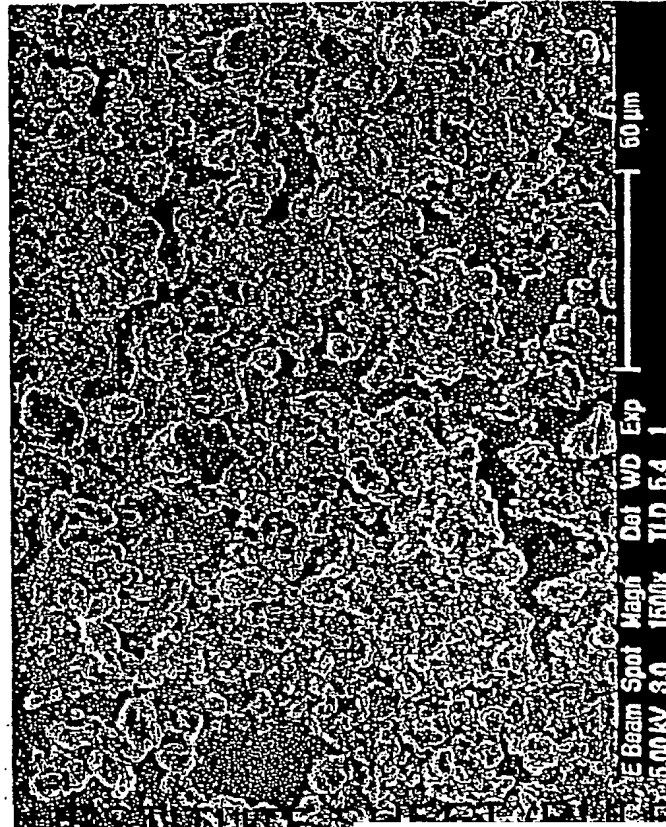


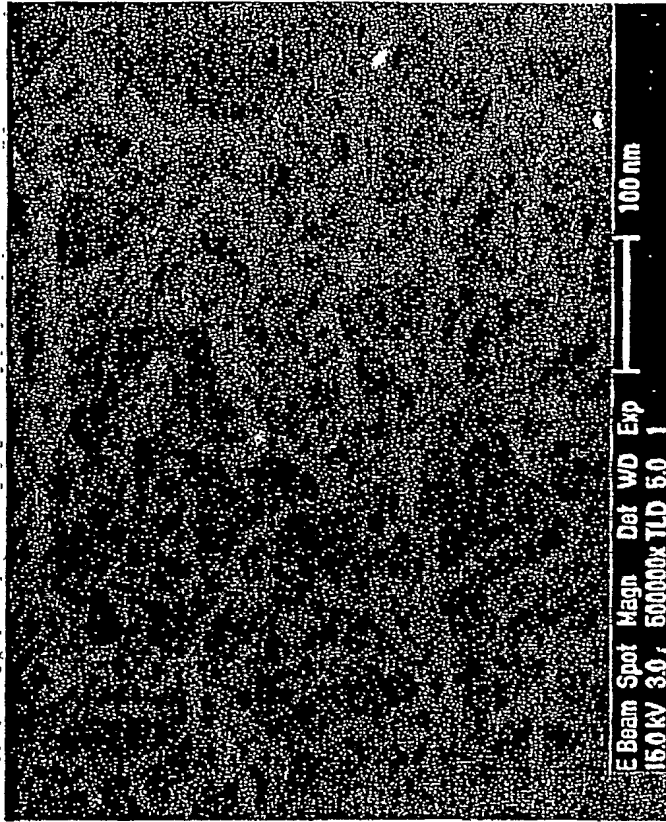
FIG. 11

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SEM VIEWS OF CNT ON A1



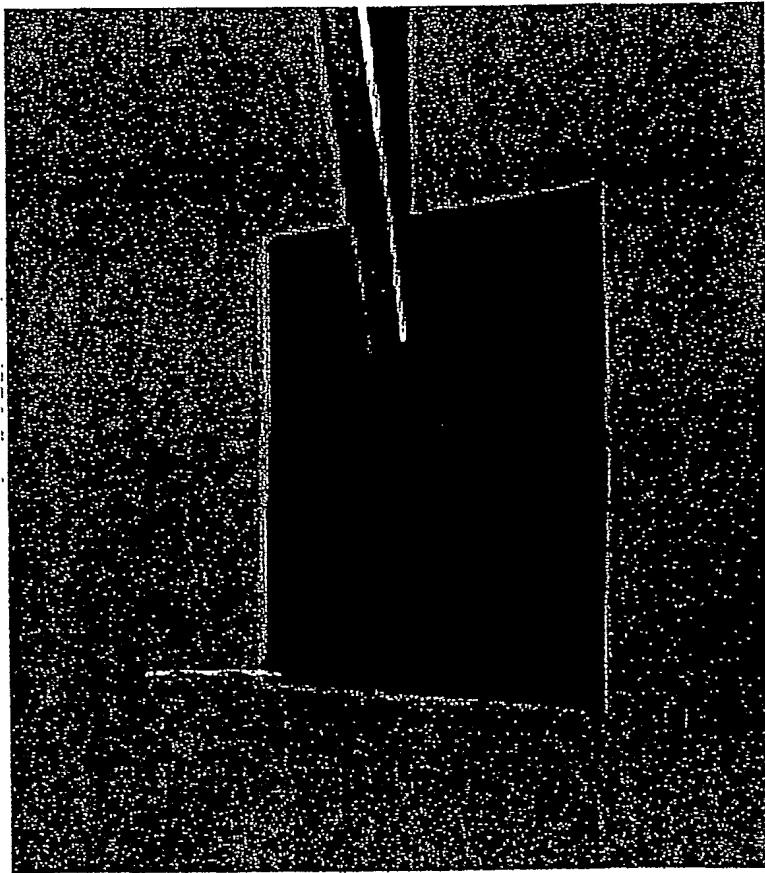
X 1,500



X 500,000

FIG. 12

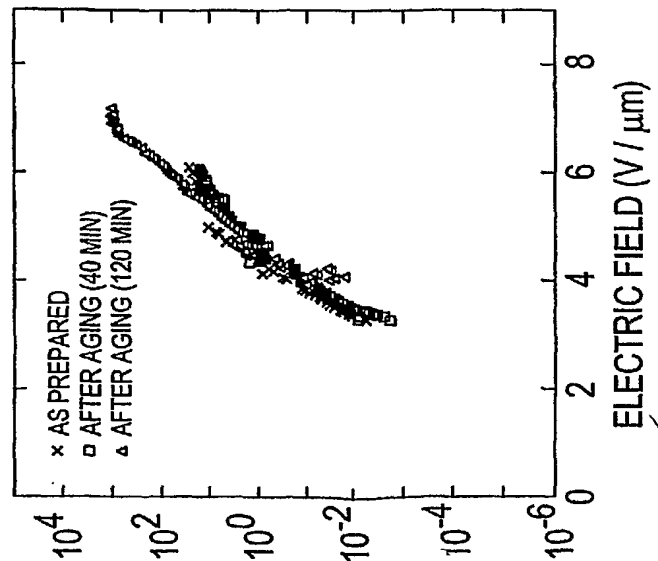
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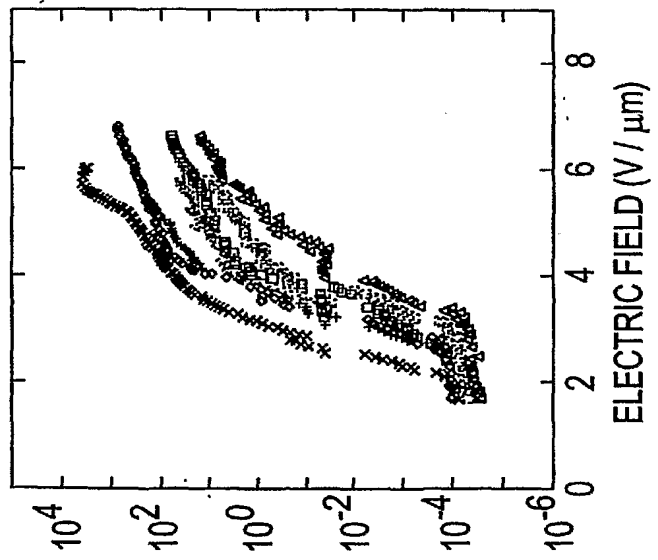
CNT-MAT

FIG. 13

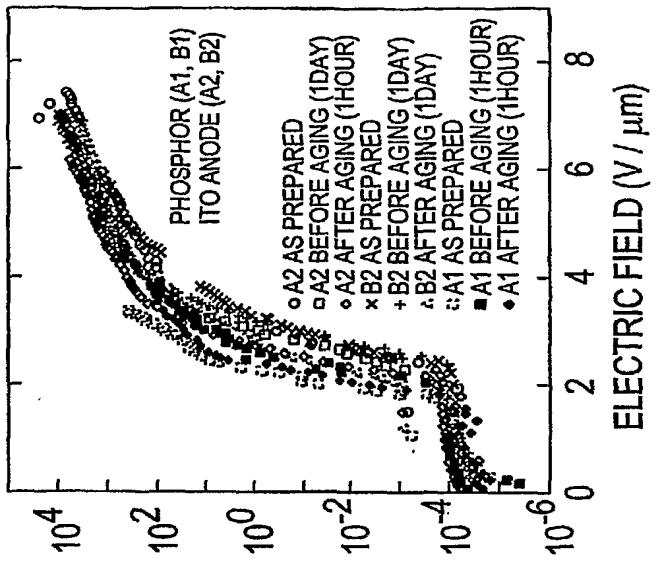
# ELECTRON EMISSION BEHAVIOR



ELECTROPHORESIS



SCREEN PRINTING



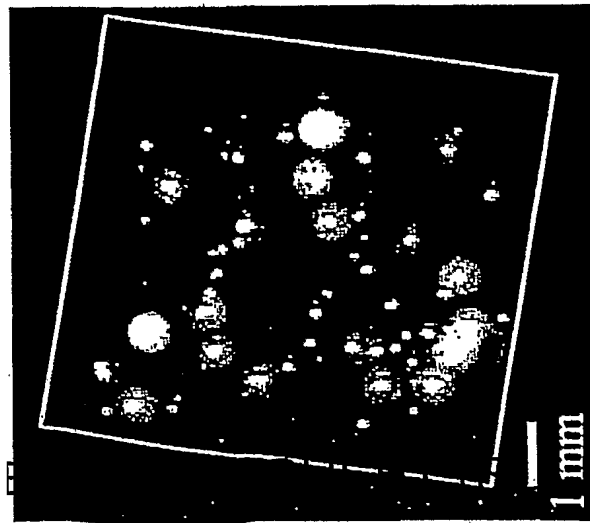
CNT-MAT

FIG. 14

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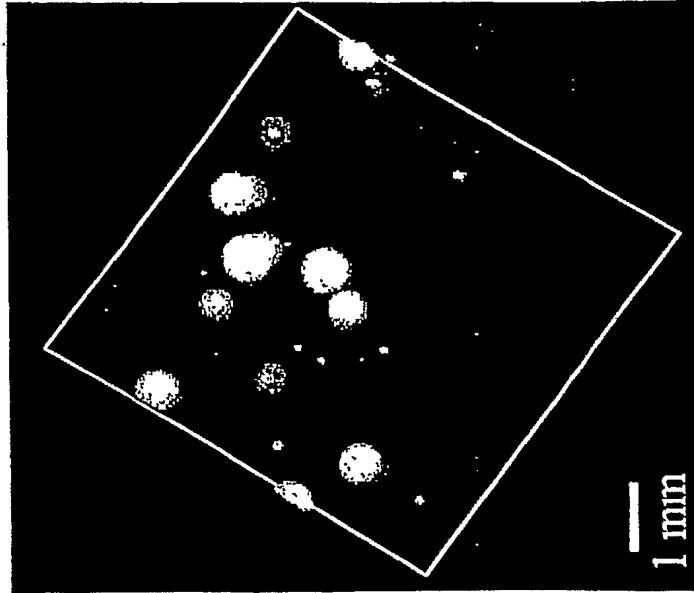
# ELECTRON EMISSION PATTERNS

ELECTROPHORESIS



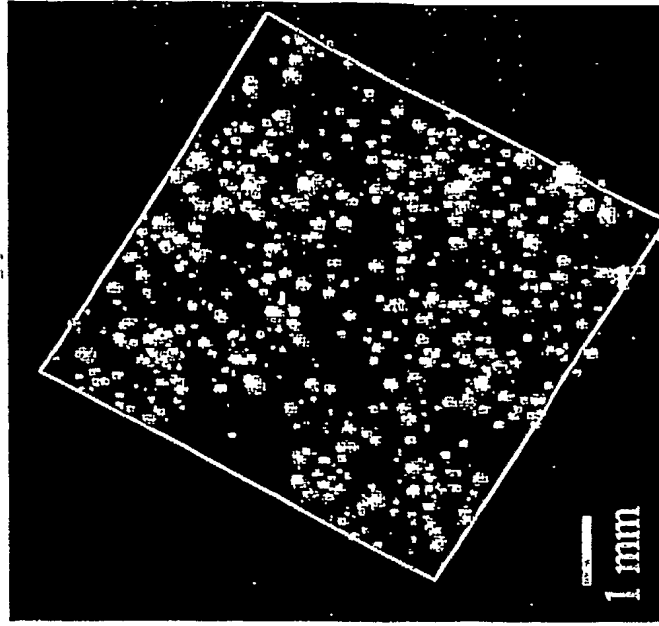
APPLIED FIELD 11.1 V/ $\mu$ m  
EMISSION CURRENT 230  $\mu$ A  
CURRENT DENSITY 639  $\mu$ A/cm<sup>2</sup>

SCREEN PRINTING



7.1 V/ $\mu$ m  
284.5  $\mu$ A  
790  $\mu$ A/cm<sup>2</sup>

CNT-MAT



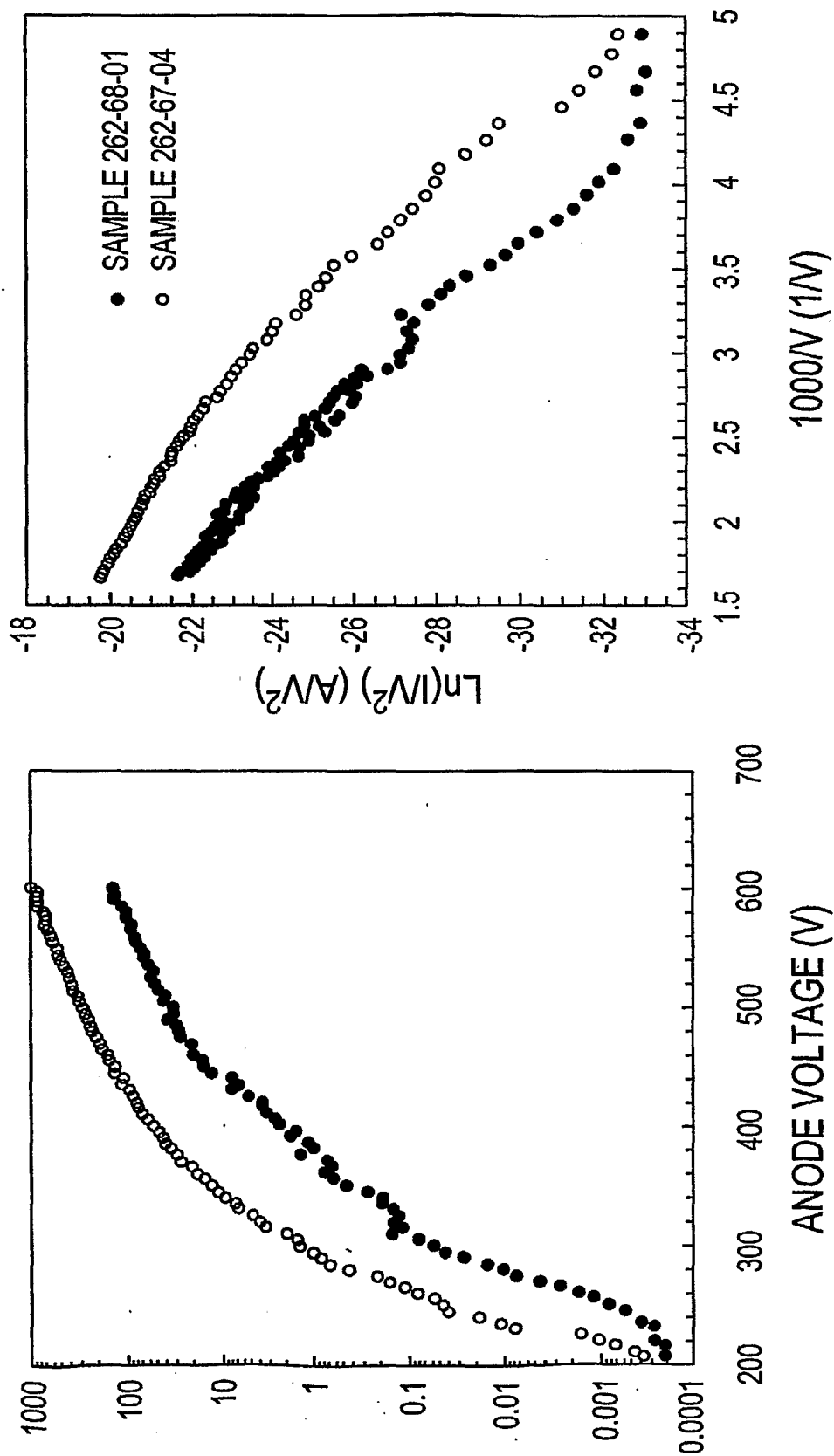
3.8 V/ $\mu$ m  
145  $\mu$ A  
402  $\mu$ A/cm<sup>2</sup>

FIG. 15



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# EMISSION CHARACTERISTICS OF INKJET PRINTED CNT

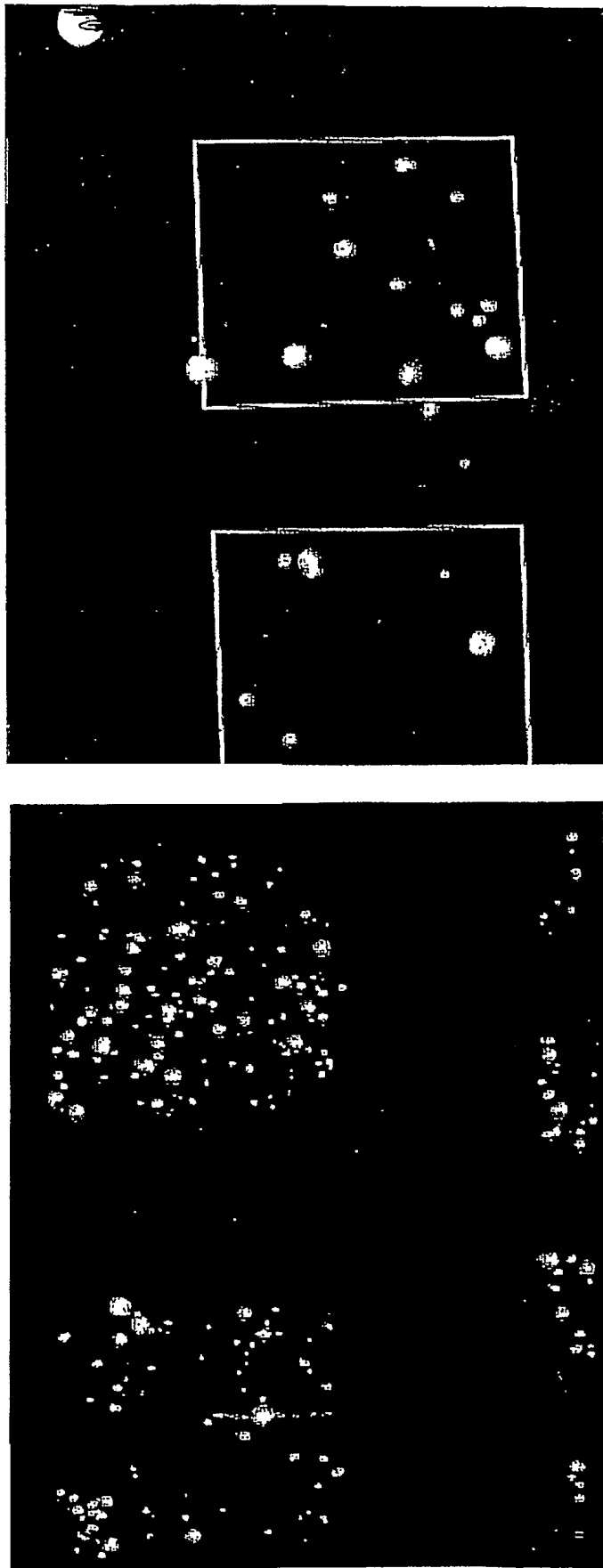


GAP BETWEEN CATHODE AND ANODE IS 150  $\mu\text{m}$

FIG. 16

EMISSION PATTERNS FROM INKJET PRINTED CNT

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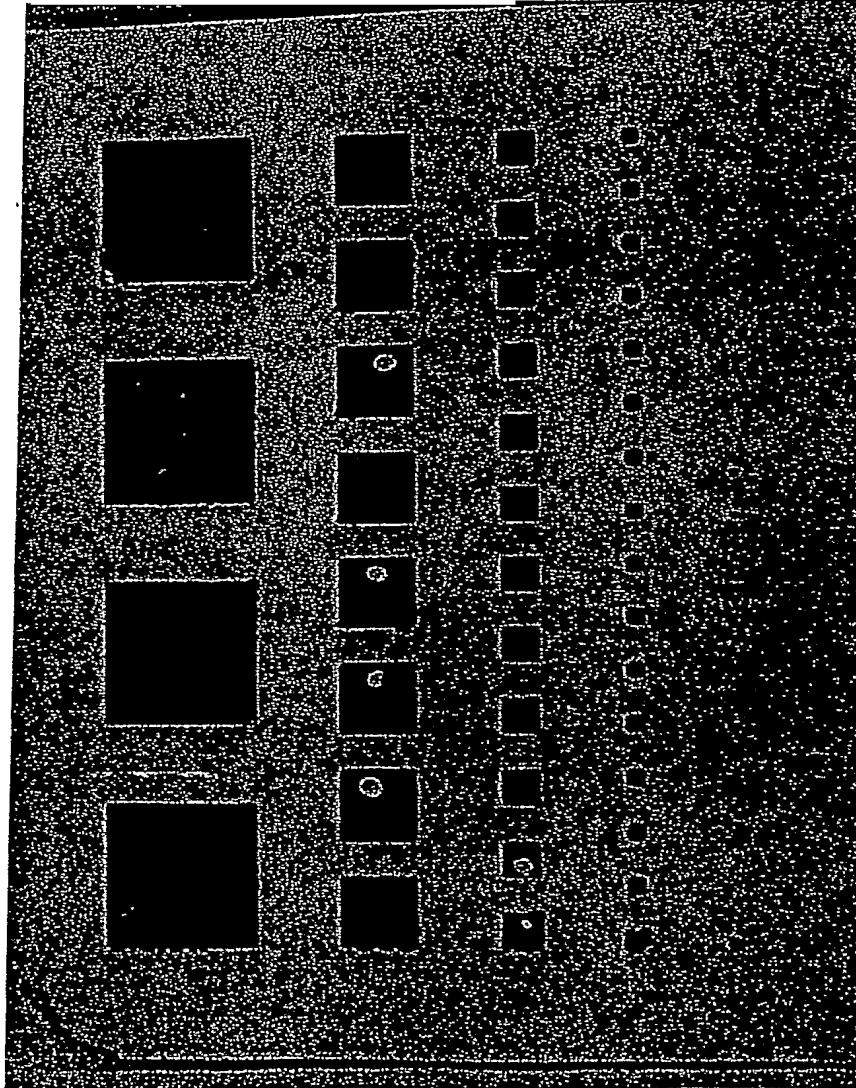
SAMPLE 262-68-01

SAMPLE 262-67-04

FIG. 17

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INKJET PRINTED CNT CATHODE

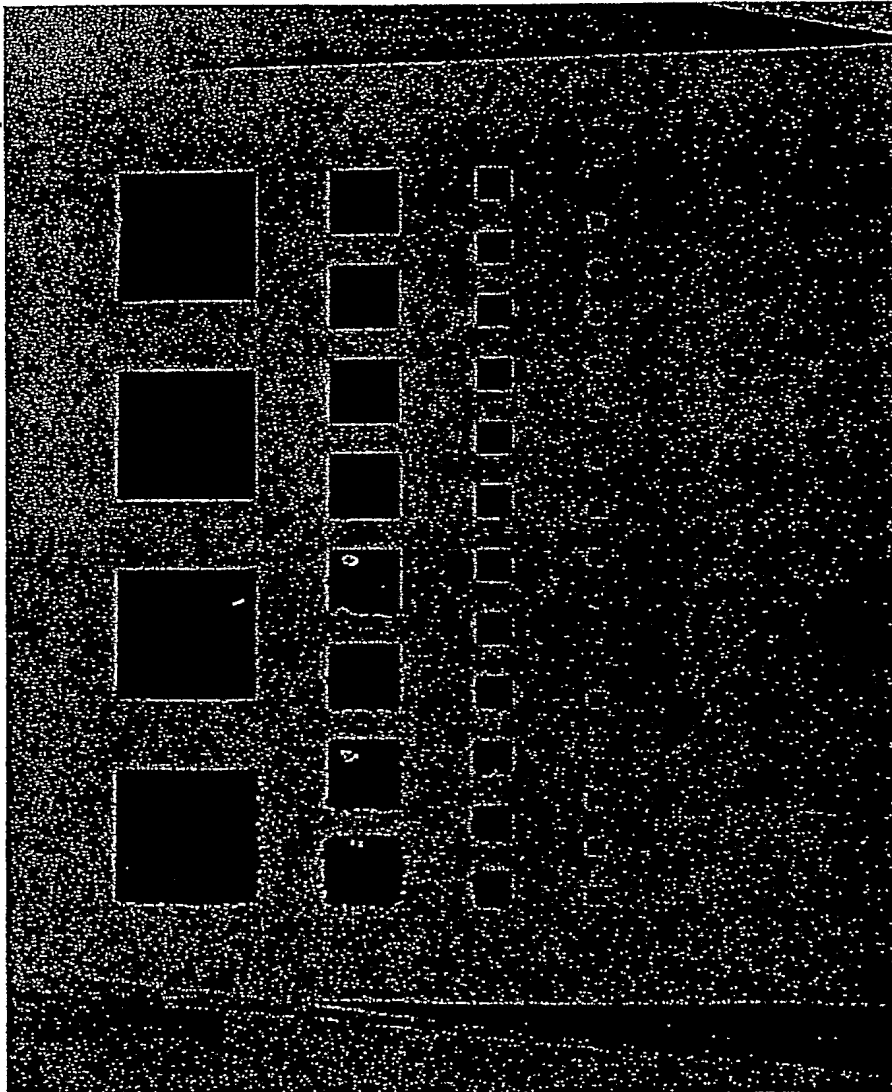


SAMPLE 262-67-01

FIG. 18

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INKJET PRINTED CNT CATHODE

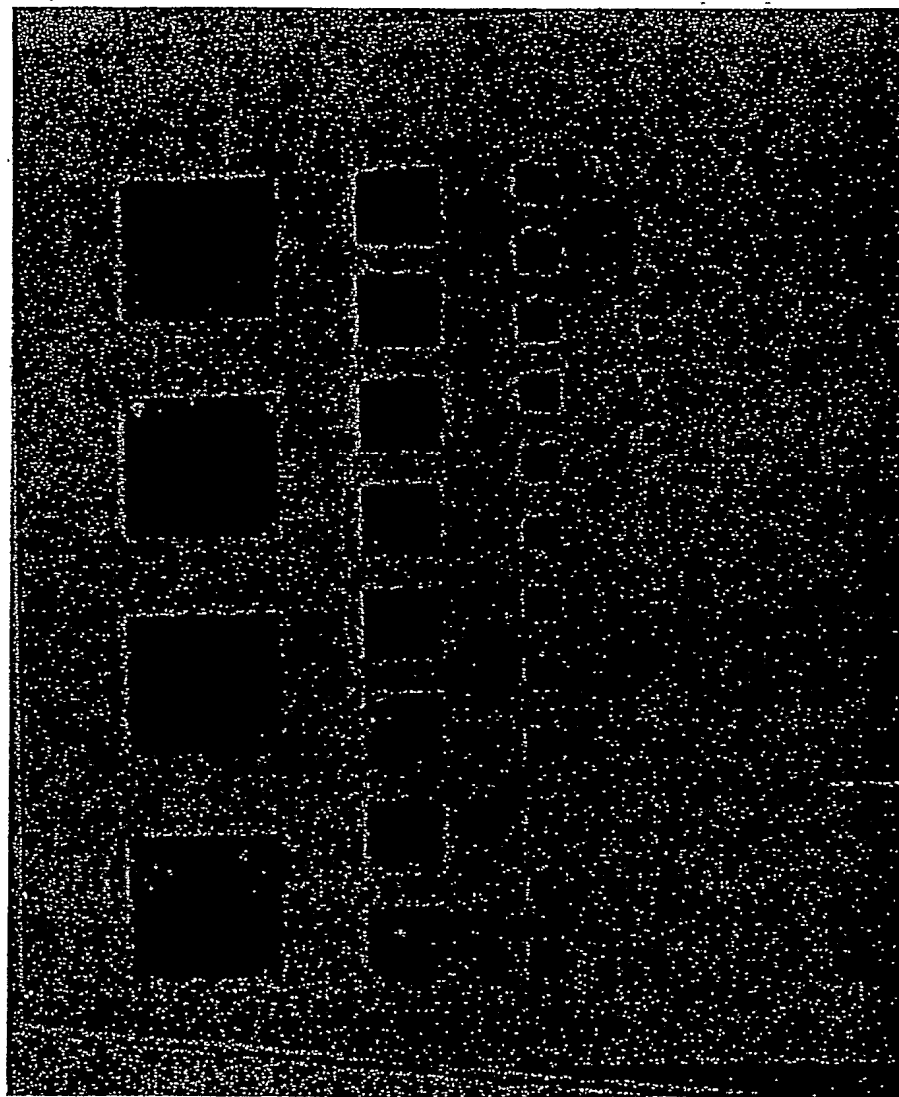


SAMPLE 262-67-02

FIG. 19

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INKJET PRINTED CNT CATHODE

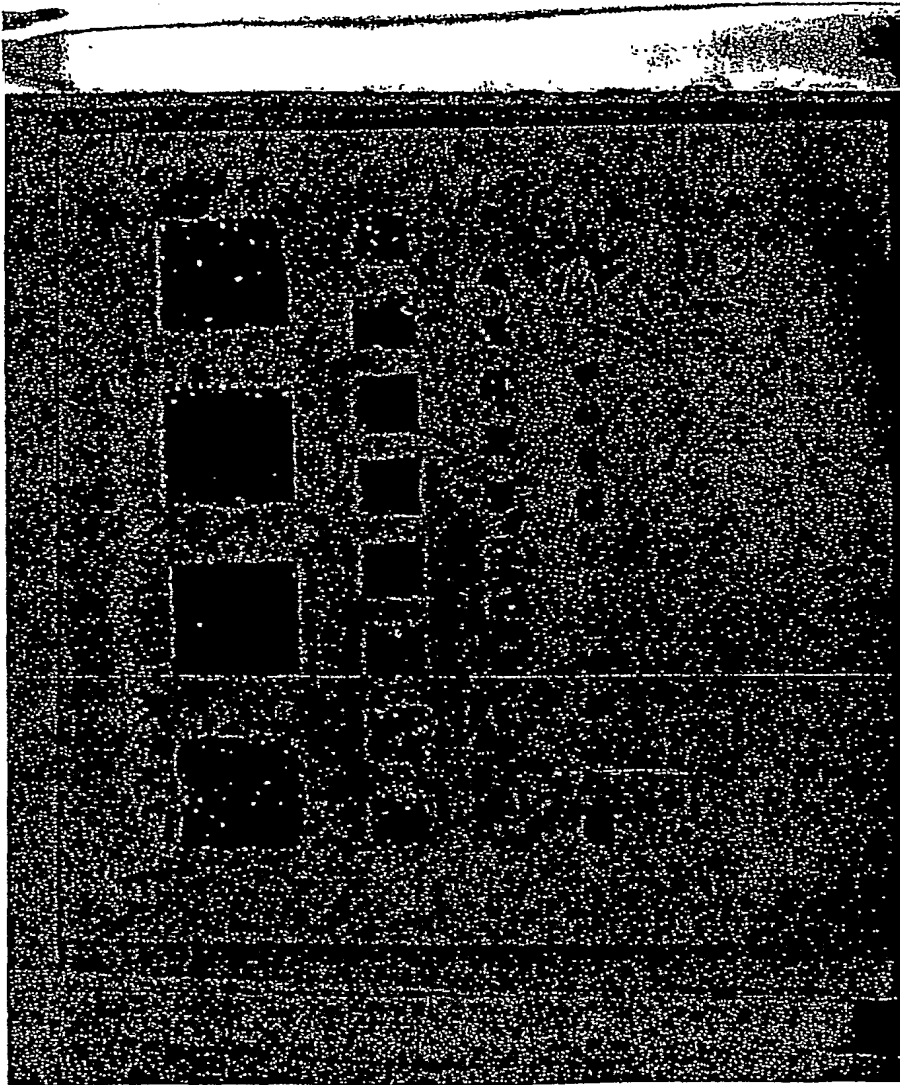


SAMPLE 262-67-04

FIG. 20

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INKJET PRINTED CNT CATHODE



SAMPLE 262-68-01

FIG. 21